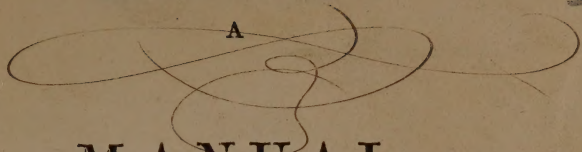


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MANUAL

OF

CHEMISTRY:

BY

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OF HER MAJESTY'S MINT;

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LITERARY AND PHILOSOPHICAL SOCIETY OF NEW YORK;
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OF PENNSYLVANIA, &c., &c., &c.

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MANUAL

CHEMISTRY



WILLIAM THOMAS BRADY

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WILLIAM THOMAS BRADY

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TO
CHARLES HATCHETT, Esq.,

F.R.S. L. & E., F.A.S.,

CORRESPONDING MEMBER OF THE ROYAL ACADEMY OF SCIENCES OF PARIS,

&c. &c. &c.

MY DEAR SIR,

To you, as my first Instructor in Chemistry, and as one whose Researches in the Science have raised your Name to a high Station among British Chemists, I beg leave to dedicate the following Work; trusting that you will receive it as a Testimony of the Gratitude and Respect with which I shall always remain,

Faithfully and affectionately yours,

WILLIAM THOMAS BRANDE.

ROYAL MINT,
1st May, 1841.

PREFACE.

THIS Work was originally intended as a text-book, for the use of the Chemical Students in the Royal Institution, but the reception of the first edition by the Public, its translation into French, German, and Italian, and its re-publication in America, induced me to improve and enlarge it, and to endeavour to render it more worthy of such marks of approbation.

The present Edition differs materially from its predecessors in all respects, except the general arrangement of its contents; this I have retained as in the original, under the conviction that it answers the purposes of the student: I have, in fact, re-written a large portion of the present volume; for the progress of Chemical Philosophy since the first appearance of this Work has been such, as to give a new character to some of its leading departments, and more or less to influence the theoretical as well as the practical details of almost all its branches. To this progress, the researches of my friend and colleague Professor Faraday have pre-eminently contributed: his discoveries in Electricity have so modified and extended the chemical bearings of that extraordinary power of matter, as to vie in importance with those of his great predecessor in the same school; while the skill with which he has traced out their connexion with physical phenomena, has gone far to withdraw some of the barriers between Chemical and Physical Science.

Organic Chemistry has also of late years assumed a new and striking aspect: the Atomic Theory has proved a powerful engine in removing many of the difficulties which encumbered its study; and the skilful activity with which its experimental details have been pursued by some of the ablest Chemists of Germany and France, has not only already been rewarded with a full measure of

interesting discovery, but has opened new and extended views to future inquirers.

These have been the principal sources of the recent changes in the aspect of Chemical Science; and whilst they have greatly contributed to its existing interest and importance, they present a promising picture of its future resources.

I have endeavoured, in this volume, to place before the reader a faithful outline of the present state of Chemistry, adapted chiefly for the instruction of the beginner, and for the use of the Student in this delightful branch of experimental Science: writing therefore for the uninitiated, and for the learner, much has been sacrificed to perspicuity, and to simplicity of detail. I must at the same time observe, that Chemistry is not what it was; that with whatever intention the pupil enters upon its study, it will require labour and thought to become usefully acquainted even with its elementary details; and that to reap advantages from its applications either to the purposes of the multitudinous Arts which are dependent upon it, or to the extension of the Sciences which are leagued with it, will perhaps demand more time and study than he is aware of. I believe that the depths of Chemistry are, with the aids which it now enjoys, more easily fathomed than those of most other branches of Physical Science, and am certain that it is admirably calculated to awaken and to gratify curiosity in regard to the phenomena both of Nature and of Art; but it is not now, as formerly, the bare history "of the effects of heat and mixture;" those who enter seriously upon its study must be prepared for some intellectual exertion and mental labour: they will then find that its connexion with other Sciences, with the arts of life, and the phenomena of nature, is such, as to render it at once useful and popular, and an essential in the range of a liberal education.

But, though chiefly addressed to the Student, I am not without hope that this Manual will be approved by the practical and experimental Chemist, especially by the Teacher of the Science: to such I have endeavoured to recommend it by copious references to authorities, and by abstracts of practical directions. Should it in these respects prove a work of reference worthy of his occasional consultation, another object will be answered.

In consequence of the popular applications of Chemistry, and

its extensive connexion with the useful and ornamental Arts, and with the Sciences at large, the general reader finds it often forced upon him; its terms are of frequent occurrence, and its language is in daily use: I have, therefore, added to this Work a copious Index, intended in some measure to supersede the use of a Chemical Dictionary.

In conclusion, I have to observe that the note-books of my Lectures have served as a foundation of the present volume, and that these include a miscellaneous collection of original and borrowed information: although, therefore, I have endeavoured, as far as possible, to refer to authorities, and to cite the sources of my statements, I fear that I may often have unintentionally omitted such acknowledgments. The systematic and elementary works which I have principally consulted, are those of Dr. William Henry, Dr. Thomas Thomson, Dr. Edward Turner, Professor Daniell, and Professor Graham; and of Berzelius, Dumas, Gmelin, Mitscherlich, Thenard, and Liebig; and the Dictionaries of Messrs. Aikin and Dr. Ure; together with the Transactions of the Royal Society, and the English and Foreign Journals: among the latter, the *Annales de Chimie et Physique*, and Poggendorff's *Journal*, are especially rich in original Chemical information.

In the preliminary remarks to the chapter on Simple Substances, are explained the principles of the Notation and Symbols which I have found it convenient to adopt, and my reasons for deviating a little upon these points from the high and accepted authority of Berzelius.

It must be the anxious wish of all who are conversant with our Science, that an uniform system of Symbols, Notation, and Equivalent, should be agreed upon and adhered to, and it is to be hoped that the British and Foreign Scientific Associations will seriously direct their exertions towards the attainment of so important an object.

The general method which I have adopted of representing the Atomic, Equivalent, and Percentage, composition of bodies, is that employed by Leopold Gmelin in his excellent *Handbuch der Theoretischen Chemie*; it saves repetition, and brings much information before the eye of the Student in a clear but condensed form; I insert the following statement of the composition of Nitrous

Oxide as an explanatory specimen of one of these tables, in its most general and extended form.

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
	A.	E.	Pr. Cent.	Davy.	Berzelius.	Higgins.	Vols.	Sp. Gr.	100 C.I.
Nitrogen . .	1	14	63·6	63·3	62·5	60	1·0	0·97	30·1
Oxygen . .	1	8	36·4	36·7	37·5	40	0·5	0·55	17·05
Nitrous oxide	1	22	100·0	100·0	100·0	100	1·0	1·52	47·21

The first column (I.) contains the component parts of nitrous oxide; (II.) shows that 1 atom of nitrous oxide is composed of 1 atom of nitrogen and 1 of oxygen; (III.) shows the equivalent weight of an atom of nitrogen = 14 and an atom of oxygen = 8, producing an atom of nitrous oxide = 22; (IV.) shows the composition *per cent.* calculated from the theoretical equivalents; (V.) (VI.) and (VII.) show the experimental results of the analyses of Davy, Berzelius, and Higgins, and enable us to compare them with the calculated or theoretical composition; (VIII.) shows that 1 volume of nitrogen and half a volume of oxygen, constitute 1 volume of nitrous oxide; (IX.) shows that the specific gravity of nitrogen being 0·97 and half the specific gravity of oxygen being 0·55, the specific gravity of nitrous oxide will be $0·97 + 0·55 = 1·52$; (X.) shows that the weight of 100 cubic inches of nitrogen being 30·16 grains, and of 50 cubic inches oxygen being 17·05 grains, the weight of 100 cubic inches of nitrous oxide will be 47·21 grains.

THE various chemical apparatus and implements of the laboratory which are mentioned or described in this Work, may be obtained of Mr. Newman, 122, Regent Street; of Mr. Palmer, Newgate Street; of Messrs. Watkins and Hill, Charing Cross; and at Messrs. Knights', Foster Lane, Cheap-side.

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HISTORICAL SKETCH OF THE ORIGIN AND PROGRESS

OF

CHEMICAL PHILOSOPHY.

§ I.

CHEMISTRY is that branch of natural knowledge which teaches us the properties of the elementary substances, and of their mutual combinations; it inquires into the laws which affect, and into the powers which preside over their union; it examines the proportions in which they combine, and the modes of separating them when combined; and endeavours to apply such knowledge to the explication of natural phenomena, and to useful purposes in the arts of life*.

Chemistry cannot be said to have existed, as a science, previous to the commencement of the seventeenth century; for although we find, in the writings of the earlier chemists, many curious and important facts and discoveries, these remained useless and unapplied, so long as the minds of men were exclusively directed to the transmutation of the metals, the composition of an universal elixir, and the production of the *Alcahest*, or general solvent. Although, therefore, it may often be amusing, and sometimes profitable, to revert to the crude speculations and waking dreams of the voluminous writers upon these subjects, who were eminent in the fourteenth and two successive centuries, the time of the student will be more usefully occupied in tracing the labours of those who, discarding visionary hypotheses, proceeded to the investigation of truth;

* *Definitions of Chemistry.*—"La Chymie est un art qui enseigne à séparer les différentes substances qui se rencontrent dans un mixte." L'EMERY, *Cours de Chymie*.

"Chemistry is that science which examines the constituent parts of bodies, with reference to their nature, proportions, and method of combination." BERGMAN, *Essay on the Usefulness of Chemistry*.

"Chemistry is the study of the effects of heat and mixture, with a view of discovering their general and subordinate laws, and of improving the useful arts." BLACK, *Lectures*.

"La Chimie est une science qui apprend à connaître l'action intime et réciproque de tous les corps de la nature, les uns sur les autres. Par les mots *action intime*, et *reciproque*, cette science est distinguée de la physique expérimentale, qui ne considère que les propriétés extérieures des corps doués d'un volume,

et d'une masse qu'on peut mesurer, tandis que la Chimie ne s'attache qu'aux propriétés intérieures, et n'agit que sur des molécules, dont le volume et la masse ne peuvent pas être soumis aux mesures et aux calculs." FOURCROY, *Système des Connoissances Chimiques*, vol. i., p. 4.

"Die Chemie ist eine Wissenschaft die uns die wechselseitige wirkungen der einfachern Stoffe in der Natur, die zusammensetzung der körper aus ihren und nach ihren verschiedenen verhältnissen, und die Art und Weise kennen lehrt, sie zu trennen, oder sie wieder zu neuen Körperarten zu verbinden." GREN. *Systematisches handbuch der Chemie*, p. 1. Halle, 1794.

"Chemistry is that science which treats of those events or changes in natural bodies, which are not accompanied by sensible motions." THOMSON, *System of Chemistry*, 5th edition, p. 2.

"Most of the substances belonging to our globe are constantly undergoing

and who were led on, not by the vague glimmering of speculative notions, but by the steady daylight of real philosophy*.

It is, I think, among our own countrymen that we discover the fathers of chemical philosophy: for BACON, BOYLE, HOOKE, MAYOW, and NEWTON, present unequivocal claims to that distinctive title. As induction from experiment is exclusively the basis of chemical science, little progress could be made in it till the futility of the ancient philosophical systems had been shown, and their influence annihilated; till the true end of science was rightly defined, [and the road to it rendered straight and passable; till the necessity of well-digested experiment had been established, which "first procures the light, then shows the way by its means."

It may seem trite to quote Lord BACON; but, as experience is constantly showing the neglect of the invaluable doctrines inculcated in his

alterations in sensible qualities, and one variety of matter becomes, as it were, transmuted into another. Such changes, whether natural or artificial, whether slowly or rapidly performed, are called chemical; thus the gradual and almost imperceptible decay of the leaves and branches of a fallen tree exposed to the atmosphere, and the rapid combustion of wood in our fires, are both chemical operations.

"The object of chemical philosophy is to ascertain the causes of all phenomena of this kind, and to discover the laws by which they are governed." DAVY, *Elements of Chemical Philosophy*, p. 1.

In the latest editions of Johnson's *Dictionary*, the erroneous and antiquated definition of Boerhaave is very improperly retained. "An art whereby sensible bodies, contained in vessels, or capable of being contained therein, are so changed by means of certain instruments, and principally fire, that their several powers and virtues are thereby discovered, with a view to philosophy or medicine."

The derivation of the word Chemistry can scarcely be said to have been ascertained. The most plausible guesses are the following: from *χυνω*, to melt, or *χυμος*, juice; from *kema*, an oriental word signifying *black*; from *Χημης*, the name of a person eminently skilled in the sciences; from *Chémi*, the Coptic name of Egypt, where the art is supposed to have had its rise.

According to Bryant (*Ancient Mythol.*), it is derived from *chemia*, and that word from *Cham*.

The Rev. Mr. Palmer, Professor of Arabic at Cambridge, has given the following etymology: "Al-chemy, or

more properly Al-kemy, the knowledge of the substance or composition of bodies, so named from the substantive (Kya-mon), that is the substance or constitution of anything; from the root (Kama.) Golius. *Lexicon*." THOMSON'S *Chemistry*, 5th edit., p. 4, Note.

Conversing upon this subject with my late friend, Dr. Thomas Young, he remarked, that the Egyptians probably neither knew nor cared much about the composition of bodies; and that the term Chemistry, as referring to the secret art of transmutation, was probably derived from the Coptic root *hheims* or *chems*, signifying *obscure*, *dark*. The German word *geheim*, *secret*, he said, was perhaps of the same root.

"Hæc ars varia accepit nomina, nam omnium primò dicta fuit τέχνη ποιητική, et antiquis illis temporibus per hanc vocem significabant artem villa metalla in aurum convertendi, et ejus artifices ποιηταί vocari Zozimus dicit. Veteres Ægyptios hanc artem Chimoet vocasse Josephus Scaliger ibi ostendit, sed postea Græci hanc artem χυμοποιαν dixerunt, Arabibus vero, Alchemia." BOERHAAVE, *Institutiones Chemicæ*.

* "Tout ce qu'on a dit de l'antique origine de la Chimie, sur les premiers hommes qui ont travaillé les métaux, taillé et poli les pierres dures, fondu les sables, dissous et cristallisé les sels, ne montre à un esprit exact et sévère qu'une vaine et ridicule prétension, semblable à cette par laquelle on voudrait reconnoître les élémens de la géométrie dans l'ouvrage grossier du sauvage qui use les fragmens du rocher, qui leur donne des formes à peu près régulières pour les rendre utiles à ses premiers besoins." FOURCROY, *Discours Préliminaire*.

works, and as students, especially, are too apt to throw off the burden and responsibility of thinking for themselves, by adopting the notions of others, without duly weighing their merit or appreciating their correctness, and often only because they are new, I shall call their attention to one of the many relevant passages of this author:—

“He who would come duly prepared, and fitted to the business of interpretation, must neither be a follower of novelty, custom, nor antiquity; nor indulge himself in a liberty of contradicting; nor servilely follow authority. He must neither be hasty in affirming, nor loose and sceptical in doubting; but raise up particulars to the places assigned them by their degree of evidence and proof. His hope must encourage him to labour, and not to rest; he must not judge of things by their uncommon nature, their difficulty, or their high character; but by their just weight and use. He must, in his own particular, carry on his view with concealment, and yet have a due regard for posterity. He must prudently observe the first entrance of errors into truths, and of truths into errors, without despising or admiring anything. He must understand his own talents and abilities, or the advantages of his own nature. He must comply with the nature of others. He must, as with one eye, survey the natures of things, and have the other turned towards human uses. He must distinctly understand the mixed nature of words, which is extremely capable both of prejudicing and assisting. He must lay it down to himself, that the art of discovering will grow up, and improve, along with discoveries themselves. He must not be vain either in delivering or concealing the knowledge he has acquired, but ingenuous and prudent, and communicate his inventions without pride or ill-nature: and this in a strong and lively manner, well defended against the injuries of time, and fit for the propagation of knowledge, without occasioning errors; and, which is the principal thing of all, it must be such as may select and choose for itself a prepared and suitable reader*.”

The following observations, from the same source, bring us back to our subject:—

“And again; if any one should condescend to regard such things as are accounted rather curious than useful, and take a thorough view of the works of the alchymists, or the followers of natural magic, he might, perhaps, be at a difficulty which he should withhold, his tears, or his laughter. For the alchymist goes on with an eternal hope; and where his matters succeed not, lays the blame upon his own errors; and accuses himself as not having sufficiently understood either the terms of his art, or his author: whence he either hearkens out for traditions and auricular whispers, or else fancies he made some mistake as to the exact quantity of the ingredients, or nicety of the experiment; and thus repeats the operation without end. And if, in the mean time, among all the chances of experiments, he throws any which appear either new or useful, he feeds his mind with these as so many earnest; boasts and extols them above measure; and conceives great hopes of what is behind. It must, indeed, be allowed that the alchymists have made many discoveries, and obliged mankind with useful inventions; but they are well represented in that fable of the old man, who left an estate to his children, buried

* *Prefatory Aphorisms of the Novum Organum Scientiarum.* No. XI.

somewhere or other, he told them, in his vineyard; which they, therefore, fell to dig for with great diligence; whereby, though they found no gold in substance, yet they received a better vintage for their labour.

"But such as apply to natural magic, and explain everything by sympathies and antipathies, have, by supine and indolent conjectures, placed strange virtues and operations in things; and if, at any time, they have produced works, they are rather suited to admiration and strangeness, than to fruit and advantage*."

It is my intention, in this introductory chapter, after a brief allusion to the style and views of the alchemical writers, to notice the principal researches of the chemists of the fifteenth and two following centuries; and thus to give an historical sketch of the science, from its early days, to the commencement of the present age.

In reference to the ends and objects of chemical science, under its present aspect, I cannot do better than quote our modern Bacon, from whose *Discourse on the Study of Natural Philosophy*, I shall be content with the following extract, earnestly advising all students steadily to peruse and consider that excellent and sensible essay:—

"The laws," says Sir F. W. HERSCHEL, "which concern the intimate constitution of bodies, not as respects their *structure* or the manner in which their parts are put together, but as regards their *materials* or the ingredients of which those parts are composed, form the objects of chemistry. A solid body may be regarded as a fabric, more or less regularly and artificially constructed, in which the materials and the workmanship may be separately considered, and in which, though the latter be ruined and confounded by violence, the former remain unchanged in their nature, though differently arranged. In liquid or aerial bodies, too, though there prevails a less degree of difference in point of structure, and a greater facility of dispersion and dissipation, than in solids, yet an equal diversity of *materials* subsists, giving to them properties differing extremely from each other.

"The inherent activity of matter is proved not only by the production of motion by the mutual attractions and repulsions of distant or contiguous masses, but by the changes and apparent transformations which different substances undergo in their sensible qualities by mere mixture. If water be added to water, or salt to salt, the effect is an increase of quantity, but no change of quality. In this case, the mutual action of the particles is entirely mechanical. Again, if a blue powder and a yellow one, each perfectly dry, be mixed and well shaken together, a green powder will be produced: but this is a mere effect arising in the eye from the intimate mixture of the yellow and blue light separately and independently reflected from the minute particles of each; and the proof is had by examining the mixture with a microscope, when the yellow and blue grains will be seen separate and each quite unaltered. If the same experiment be tried with coloured liquids, which are susceptible of mixing without chemical action, a compound colour is likewise produced, but no examination with magnifiers is in that case sufficient to detect the ingredients; the reason obviously being, the excessive minuteness of the parts, and their perfect intermixture, produced by agitating

* *Novum Organum*, Section V.

two liquids together. From the mixture of two powders, extreme patience would enable any one, by picking out with a magnifier grain after grain, to separate the ingredients. But when liquids are mixed, no mechanical separation is any longer practicable; the particles are so minute as to elude all search. Yet this does not hinder us from regarding such a compound as still a mere mixture, and its properties are accordingly intermediate between those of the liquids mixed. But this is far from being the case with all liquids. When a solution of potash, for example, and another of tartaric acid, each perfectly liquid, are mixed together in proper proportions, a great quantity of solid saline substance falls to the bottom of the containing vessel, which is quite different from either potash or tartaric acid, and the liquid from which it subsided offers no indications by its taste or other sensible qualities of the ingredients mixed, but of something totally different from either. It is evident that this is a phenomenon widely different from that of mere mixture; there has taken place a great and radical change in the intimate nature of the ingredients, by which a new substance is produced which had no existence before. And it has been produced by the *union* of the ingredients presented to each other; for when examined it is found that nothing has been *lost*, the weight of the whole mixture being the sum of the weights mixed. Yet the potash and tartaric acid have disappeared entirely, and the weight of the new product is found to be exactly equal to that of the tartaric acid and potash employed, taken together, abating a small portion held in solution in the liquid, which may be obtained, however, by evaporation. They have therefore combined, and adhere to one another with a cohesive force sufficient to form a solid out of a liquid; a force which has thus been called into action by merely presenting them to each other in a state of solution.

“It is the business of chemistry to investigate these and similar changes, or the reverse of such changes, where a single substance is resolved into two or more others, having different properties from it, and from each other, and to inquire into all the circumstances which can influence them; and either determine, modify, or suspend their accomplishment, whether such influence be exercised by heat or cold, by time and rest, or by agitation or pressure, or by any of those agents of which we have acquired a knowledge, such as electricity, light, magnetism, &c.”

§ II.

THE transmutation of baser metals into gold and silver, which was the chief, and, in most cases, the only object of the genuine alchemists, was not merely regarded as possible, but believed to have been performed, by some of the more enlightened chemists of the seventeenth century; and in perusing the history of these transmutations, as recorded by HELVETIUS, BOERHAAVE, BOYLE, and other sober-minded men, it would be difficult to resist the evidence adduced, without the aids of modern science. Lord BACON'S sound sense has been arraigned for his belief in alchemy, though he, in fact, rather urges the possibility than the probability of transmutation; and, considering the infant state of the experimental sciences, and of chemistry in particular, in his age, and the plausible

exterior of the phenomena that the chemists were able to produce, he is rather to be considered as sceptical than credulous, upon many of the points which he discusses.

HERMES TRISMEGISTUS, who is said to have lived in the year of the world 2076, has generally been quoted as the oldest of the alchemists; there can, however, be very little doubt that the writings attributed to him are entirely spurious. The *Tractatus Aureus*, or *Golden Work*, is evidently a farrago of occult philosophy belonging to a much later period. HERMES, at the outset, is made to apologize for divulging the secrets of the black art. "I should never have revealed them," says he, "had not the fear of eternal judgment, or the hazard of the perdition of my soul, prevailed with me, for such a concealment. It is a debt I am willing to pay to the just, even as the Father of the just liberally bestowed it upon me." After this prelude, we might expect to be let into some of the mysteries of alchemy, but our curiosity is quickly disappointed, by finding that they are only revealed to the eyes and ears of the sons of art; "not to the profane, the unworthy, and the scoffers, who, being as greedy dogs, wolves, and foxes, are not to feed at our divine repast." The reader is then conducted into what is termed the *innermost chamber*, and regaled with a history and explanation of various matters relating to the philosopher's stone, by means of which, "through the permission of the Omnipotent, the greatest disease is cured, and sorrow, distress, evil, and every hurtful thing evaded; by help of which we pass from darkness to light, from a desert and wilderness to a habitation and home, and from straitness and necessities to a large and ample estate." We are then directed to "catch the flying bird," by which is meant quicksilver; "and drown it so that it may fly no more;" this is what is afterwards termed the *fixation* of mercury, by uniting it to gold. It is then to be plunged into the "well of the philosophers," or *aqua regia*, "by which its soul will be dissipated, and its corporeal particles united to the "red eagle," or muriate of gold.

GEBER is another great name in the history of alchemy*; the exact period at which he lived is unknown, but it was probably not later than the seventh century. Whatever may be the date or the authenticity ascribed to the works bearing the name of GEBER, they are among the oldest chemical treatises in existence, and merely as such deserve the perusal of the historian. His three books of alchemy were published at Strasburgh, in 1520, and, if genuine, contain matter that justifies the praise of BOERHAAVE, who considers him as a first-rate philosopher of his age. In his chapter *On the Alchemie of Sol*, after descanting upon the different means of refining and dissolving gold, he describes several solar

* "Primus omnium Arabum post Græcos est Geber, cui dant titulum Arabis. Alii dicunt eum fuisse regem, unde *rex Geber Arabs*, dici solet; sed *Leo Africanus*, qui Græcus fuit et multa descripsit ex antiquis Arabibus, dicit Gebrum illum natione Græcus fuisse, sed derogasse suam religionem, et se dedisse Mahomedæ religioni Arabum, et vixisse septimo seculo." BOERHAAVE.

Geber was also a physician and astronomer. The following are the principal works on chemistry which have been attributed to him: *De Alchemia*,—*De summa Perfectione Metallorum*,—*De Lapide Philosophico*,—*De inveniendi Arte Auri et Argenti*. These, and some other works bearing his name, whether genuine or not, furnish good specimens of the early alchemical writings.

medicines in language which is tolerably intelligible; they are all solutions of gold in nitro-muriatic acid, with the addition of quicksilver, nitre, common salt, and some other saline matters. The student is directed to prepare his mind for his pursuits by suitable acts of piety and charity, which, if earnestly and perseveringly carried on, may, after due time, enable him, "to change argent vive into an infinite solific and lunific, without the help of anything more than its multiplication." Alembics, crucibles, and various furnaces are so fully described, and, if we may believe the MSS., depicted by GEBER, that he deserves to be mentioned also as the inventor of much useful apparatus. Some have asserted his pretensions to the possession of the universal medicine, for he speaks of curing disease; but this seems a mere metaphorical expression, relating to transmutation. "Bring me," says he, "the six lepers, that I may cleanse them;" by which he probably would imply the conversion of silver, mercury, copper, iron, tin, and lead, into gold; these seven metals only having been known at that period. Dr. Johnson supposes that the word *Gibberish*, anciently written *Geberish*, was originally applied to the language of Geber and his tribe.

ARTEPHIUS, in 1130, published several alchemical tracts: we are told by ROGER BACON and others, that he died at the age of 1025, having prolonged his life by the miraculous virtues of his medicines; but his name, and that of JOHN DE RUPESCISSA, are now deservedly forgotten.

The alchemical annals of the thirteenth century are adorned by the name of ROGER BACON, a native of Ilchester, in Somersetshire, and descended from an ancient and honourable family. In 1240, he returned from Paris, and became celebrated among the learned of the University of Oxford. At that time, however, the exposition of ignorance, and attempts to overthrow the dogmas of the schools, was a service of risk and danger; and to this Friar BACON, for he was a monk of the Franciscan order, laid himself fully open: he was accused of practising witchcraft, thrown into prison, and nearly starved, for exposing the prevalent immorality of the clergy; and, according to some, stood a chance of being burned as a magician.

I know of no work that strikes one with more surprise than the *Opus Majus* of ROGER BACON; he stands alone like a beacon upon a waste; he is perspicuous and comprehensive; and full of anticipations of the advantages likely to be derived from the mode of investigation insisted upon by his great successor, Chancellor BACON. This resemblance between ROGER BACON and his illustrious namesake has scarcely been noticed by the historians of his period; it has, however, not escaped Mr. HALLAM'S observation, who adverts to it in his *History of the Middle Ages*. Whether Lord BACON, he says, "ever read the *Opus Majus*, I know not; but it is singular, that his favourite quaint expression, *prærogative scientiarum*, should be found in that work; and whoever reads the sixth part of the *Opus Majus*, upon experimental science, must be struck by it as the prototype in spirit of the *Novum Organum*. The same sanguine and sometimes rash confidence in the effect of physical discoveries; the same fondness for experiment; the same preference of inductive to abstract reasoning, pervade both works."

The alchemical work of ROGER BACON which has been most prized, is the *Mirror of Alchymy*, but there is little either of interest or entertainment to be extracted from it*.

ROGER BACON has by some been spoken of as a benefactor to mankind, by others as an enemy to the human race, inasmuch as he is plausibly considered to have invented gunpowder†, an invention by which the personal barbarity of warfare has certainly been diminished, "but which, considered as an instrument of human destruction, by far more powerful than any that skill had devised, or accident presented, before; acquiring, as experience shows us, a more sanguinary dominion in every succeeding age, and borrowing all the progressive resources of science and civilization for the extermination of mankind, appals us," says Mr. HALLAM, "at the future prospects of the species, and makes us feel, perhaps more than in any other instance, a difficulty in reconciling the mysterious dispensation with the benevolent order of Providence."

This discovery has sometimes been given to BARTHOLOMEW SCHWARTZ, a German monk, and the date of 1320 annexed to it, a date posterior to that which may be justly claimed for Friar BACON. Upon the authority, however, of an Arabic writer in the Escorial collection, referred to by Mr. HALLAM, there seems little reason to doubt that gunpowder was introduced, through the means of the Saracens, into Europe, before the middle of the fifteenth century, though its use in engines of war was probably more like that of fireworks than artillery. Many authorities might be adduced to prove the common use of gunpowder early in the fourteenth century. EDWARD THE THIRD employed artillery with memorable effect at the battle of Cressy; and, in the fifteenth century, hand-cannons and muskets came into use, and gunpowder was in common employ.

ALBERT OF COLOGNE, surnamed THE GREAT, was a contemporary of ROGER BACON; he is celebrated as the inventor of the *brazen head*, which

* Gmelin has given the following list of the chemical writings of Roger Bacon. The two first are given in Mangetus.

1. Speculum Alchymiaë.
2. Epistola de Secretis Operibus Artis et Naturæ, et de Nullitate Magiæ.
3. De Mirabili Potestate Artis et Naturæ.
4. Medulla Alchymiaë.
5. De Arte Chemiæ.
6. Breviarium Alchymiaë.
7. Documenta Alchymiaë.
8. De Alchymistarum Artibus.
9. De Secretis.
10. De Rebus Metallicis.
11. De Sculpturis Lapidum.
12. De Philosophorum Lapide.
13. Opus Majus, or Alchymia Major.
14. Breviarium de Dono Dei.
15. Verbum Abbreviatum de Leone Viridi.
16. Secretum Secretorum.

17. Tractatus Trium Verborum.
18. Speculum Secretorum.

† "From saltpetre and other ingredients," says Roger Bacon, "we are able to form a fire which will burn to any distance." And again, alluding to its effects, "a small portion of matter about the size of the thumb, *properly disposed*, will make a tremendous sound and concussion, by which cities and armies might be destroyed." And again, in the same work, is a passage which, though somewhat enigmatical, is supposed to divulge the secret of this preparation. "*Sed tamen salis petraë, luru mone cap ubre, et sulphuris, et sic facies tonitrum si scias artificium.*" The anagram is convertible into *carbonum pulvere*. Such are the claims of Roger Bacon to a discovery which soon changed the whole art of war.

was demolished by the pious zeal of his pupil, the angelical Dr. Aquinas*, in consequence of his suspecting it to be an agent of the devil. ALBERTUS MAGNUS was what in our days is termed an universal genius. He is chiefly celebrated as the commentator of ARISTOTLE; but, if we give credit to contemporary writers, he was deeply skilled in all the higher departments of alchemical philosophy. His works, which are very voluminous, were published at Leyden, in 1651, by Peter Jammy. They fill twenty-one folio volumes. Most of his alchemical tracts have been inserted in the *Theatrum Chemicum*.

The names of RAYMOND LULLY of Majorca, and ARNOLD of Villanovat, occur in this page of the history of chemical science. Their merit, however, consists rather in the quantity than quality of their writings. LULLY died on his passage from Africa in 1315, whither he had been to preach the truths of the Gospel; his body was carried to Majorca, where he was honoured as a martyr. BRUCKER says, "he was more ingenious than honest." His chemical opinions are scarcely worth quotation or abstract. He is said to have converted iron into gold in the presence of EDWARD THE FIRST in London, which was coined into rose-nobles†.

ARNOLD shines as a magician and astrologer. He was a renowned prophet, and predicted that the world would come to an end in the year 1376. He was shipwrecked on the coast of Genoa, in 1313.

ISAAC and JOHN of Holland were also alchemical philosophers of this period§.

About the year 1560, a *Treatise of Alchymy* was published at Paris, attributed to NICHOLAS FLAMMEL. The work, however, is spurious, and was merely ascribed to him from his becoming suddenly, as it is said, very rich. The use he made of his wealth does his memory much credit: he founded hospitals, repaired churches, and endowed several charitable institutions; proceedings which by no means savour of alchemy. Dr. SALMON, who in 1692 published one of the above-mentioned tracts, says, "FLAMMEL was originally a poor scrivener, yet left so great monuments behind him, as must convince the most incredulous that he knew the secret; and performed such mighty works at his own proper cost and charges, as the most opulent prince in Europe can never do the like. I know," says he, "a gentleman who went to view those mighty buildings and their records. The archives and governors of those places, he told me, own the matter of fact, but deny the means, saying, that FLAMMEL was a very pious man, and went a pilgrimage to St. James of Gallicia,

* Thomas Aquinas wrote several works on alchemy. "So far as I have perused them," says Dr. Thomson, "they are exceedingly obscure, and in various places unintelligible. Some of the terms, still employed by modern chemists, occur for the first time in his writings. Thus the term *amalgam*, still employed to denote a compound of mercury with another metal, occurs in them. I have not observed it in any earlier author."

† Raymond Lully was born in Majorca,

in 1236, and Arnold of Villanova in Provence, in 1235.

‡ BERGMAN, *Histor. Chem.*

§ "Sequuntur nunc Johannes et Isaacus Hollandus, pater et filius, qui diffusissimo sermone et magnâ eloquentiâ scripserunt, et si unum vel alterum arcanum exceperis pulcherrima experimenta fecerunt de sanguine et urinâ humanâ, quæ Helmontius postea et Boyleus pro recentioribus inventis habuerunt."—BOERHAAVE.

for a reward of which piety the holy saint bestowed that vast treasure upon him by way of miracle; thereby denying the power of art by which it was certainly effected, to establish a miracle performed by the Romish saint." He was moreover celebrated for his hieroglyphics, of which fac-similes are given in SALMON's edition. They are much of the same cast as those that now adorn MOORE's *Almanac*, and quite as edifying.

In SALMON's collection we find the *Marrow of Alchymy*, by GEORGE RIPLEY, *Chanon of Bridlington in Yorkshire*, who was a chemist perhaps less deserving of the reputation he acquired than most of his compeers. He may be quoted as a chemical poet. His *Compound of Alchemie*, dedicated to EDWARD THE FOURTH, is rugged enough, but not unintelligible. The following stanzas from the preface of this piece, given in ASHMOLE's *Theatrum Chemicum Britannicum*, will afford a fair idea of RIPLEY's merits as a poet and philosopher:—

But into Chapters thys Treatis I shall devyde,
In number twelve, with dew recapitulatyon;
Superfluous rehearsalls I lay asyde,
Intendyng only to give trew informatyon,
Both of the theoryke and practycall operatyon:
That by my wrytyng who so wyll guyded be,
Of hys intente perfectly speed shall he.

The fyrst chapter shall be of naturall *Calcination*;
The second of *Dyssolution*, secret and phylosophycall;
The third of our elementall *Separation*;
The fourth of *Conjunction* matrimoniall;
The fyfth of *Putrefaction* then followe shall:
Of *Congelation* *Albyficative* shall be the sixt,
Then of *Cybatation*, the seaventh shall follow next.

The secret of our *Sublymation* the eyght shall show;
The nynth shall be of *Fermentatyon*;
The tenth of our *Exaltation* I trow.

The-elevent of our mervelose *Multiplycatyon*,
The twelfth of *Projection*, then *Recapitulatyon*,
And so this treatise shall take an end,
By the help of God, as I entend.

Thus here the Tract of Alchemie doth end;
Which tract was by George Ripley, Chanon, penn'd.

It was composed, writt, and signed his owne,
In anno twice seaven hundred seaventy-one.

Reader, assist him, make it thy desire
That after lyfe he may have gentle fire!—AMEN.

The degree of faith placed in alchemy was of course much shaken by the multiplied experiments which were undertaken during the seventeenth century; in general, however, those who failed attributed their ill success to any rather than the real cause. SALMON's creed is that of most of his contemporaries. "As to the great and philosophic work," says he, (meaning transmutation,) "it is my opinion and belief, that there is such a thing in nature. I know the matter of fact to be true, though the way and manner of doing it is as yet hid from me. I have been eye-witness of so much as is able to convince any man endued with rational faculties, that there is a possibility of the transmutation of metals; yet, for all these things, will not advise any man, ignorant of the power of nature and the

way of operation, to attempt the work, lest, erring in the foundation, he should suffer loss, and blame me. Without doubt it is a gift of God from above, and he that attains it must patiently wait the moving of the waters; when the destined angel moves the waters of the pool, then is the time to immerge the leprous metal, and cleanse it from all impurities."

VAN HELMONT says, "I am constrained to believe in the making of gold and silver, though I know many exquisite chemists to have consumed their own and other men's goods in search of this mystery; and to this day we see these worthy and simple labourers cunningly deluded by a diabolical crew of gold and silver sucking-flies and leeches. But I know that many will contradict this truth; one says it is the work of the devil, and another that the sauce is dearer than the meat."

BERGMAN, in summing up the evidence for and against the possibility and probability of transmutation, and founding his opinion upon the multitude of relations that have been handed down to us by different writers of apparent veracity, one or two of which I shall presently quote, observes that "although most of them are deceptive, and many uncertain, some bear such character and testimony, that, unless we reject all historical evidence, we must allow them entitled to confidence*."

For my own part, the perusal of the histories of transmutation appears to me to furnish solid ground for a diametrically opposite opinion. They are all of a most suspicious character; sometimes the fraud was open and intentional, seconded by juggling dexterity; at other times the performers deceived themselves: they purchased what was termed a *powder of projection*, prepared by the adepts, containing a portion of gold; and when they threw it into the fire with mercury, and found that portion of gold remaining in their crucible, they mistook its source. But the cases which are quoted as least exceptionable, are often exactly those which are really impossible; namely, where the weight of the powder of projection, and of the lead or other base metal taken conjointly, was exceeded by that of the gold produced. Such is HIERNES' history of PAYKUL's transmutation, who, with six drachms of lead and one of powder, produced an ingot that was coined into one hundred and forty-seven ducats; and many others. But the most celebrated history of transmutation is that given by HELVETIUS, in his *Brief of the Golden Calf; discovering the rarest Miracle in Nature, how by the smallest portion of the Philosopher's Stone a great Piece of Common Lead was totally transmuted into the purest transplendent Gold, at the Hague, in 1666*; and, as it is a luminous epitome of all that has been done on this subject, I shall briefly abridge the proceedings:—

"The 27th day of December, 1666, in the afternoon, came a stranger to my house at the Hague, in a plebeick habit, of honest gravity and serious authority, of a mean stature and a little long face, black hair not at all curled, a beardless chin, and about forty-four years (as I guess) of age, and born in North Holland. After salutation, he beseeched me with great reverence to pardon his rude accesses, for he was a lover of the Pyrotechnian art, and having read my treatise against the sympathetic powder of Sir KENELM DIGBY, and observed my doubt about the philosophic mystery, induced him to ask me if I really was a disbeliever as to

* *Opuscula*, iv. 127.

the existence of an universal medicine which would cure all diseases, unless the principal parts were perished, or the predestinated time of death come. I replied, I never met with an adept, or saw such a medicine, though I had fervently prayed for it. Then I said, surely you are a learned physician. No, said he, I am a brass-founder, and a lover of chemistry. He then took from his bosom-pouch a neat ivory box, and out of it three ponderous lumps of stone, each about the bigness of a walnut. I greedily saw and handled for a quarter of an hour this most noble substance, the value of which might be somewhere about twenty tons of gold; and having drawn from the owner many rare secrets of its admirable effects, I returned him this treasure of treasures with a most sorrowful mind, humbly beseeching him to bestow a fragment of it upon me in perpetual memory of him, though but the size of a coriander seed. No, no, said he, that is not lawful, though thou wouldest give me as many golden ducats as would fill this room; for it would have particular consequences, and if fire could be burned of fire, I would at this instant rather cast it all into the fiercest flames. He then asked if I had a private chamber whose prospect was from the public street; so I presently conducted him to my best furnished room backwards, which he entered," says HELVETIUS, (in the true spirit of Dutch cleanliness,) "without wiping his shoes, which were full of snow and dirt. I now expected he would bestow some great secret upon me, but in vain. He asked for a piece of gold, and opening his doublet showed me five pieces of that precious metal which he wore upon a green riband, and which very much excelled mine in flexibility and colour, each being the size of a small trencher. I now earnestly again craved a crumb of the stone, and, at last, out of his philosophical commiseration, he gave me a morsel as large as a rape-seed; but I said, this scanty portion will scarcely transmute four grains of lead. Then, said he, deliver it me back: which I did, in hopes of a greater parcel; but he, cutting off half with his nail, said, Even this is sufficient for thee. Sir, said I, with a dejected countenance, what means this? And he said, even that will transmute half an ounce of lead. So I gave him great thanks, and said I would try it, and reveal it to no one. He then took his leave, and said he would call again next morning at nine. I then confessed, that while the mass of his medicine was in my hand the day before, I had secretly scraped off a bit with my nail, which I projected on lead, but it caused no transmutation, for the whole flew away in fumes. Friend, said he, thou art more dexterous in committing theft than in applying medicine; hadst thou wrapt up thy stolen prey in yellow wax, it would have penetrated and transmuted the lead into gold. I then asked if the philosophic work cost much or required long time, for philosophers say that nine or ten months are required for it. He answered, Their writings are only to be understood by the adepts, without whom no student can prepare this magistry. Fling not away, therefore, thy money and goods in hunting out this art, for thou shalt never find it. To which I replied, As thy master showed it thee, so mayest thou perchance discover something thereof to me, who know the rudiments, and therefore it may be easier to add to a foundation than begin anew. In this art, said he, it is quite otherwise; for unless thou knowest the thing from head to heel, thou canst not break

open the glassy seal of HERMES. But enough; to-morrow, at the ninth hour, I will show thee the manner of projection. But ELIAS never came again; so my wife, who was curious in the art whereof the worthy man had discoursed, teased me to make the experiment with the little spark of bounty the artist had left me; so I melted half an ounce of lead, upon which my wife put in the said medicine; it hissed and bubbled, and in a quarter of an hour the mass of lead was transmuted into fine gold, at which we were exceedingly amazed. I took it to the goldsmith, who judged it most excellent, and willingly offered fifty florins for each ounce." Such is the celebrated history of ELIAS THE ARTIST and Dr. HELVETIUS.

Sir KENELM DIGBY, whose name is mentioned in this narrative, was a renowned dabbler in the mysterious art. Under the date of seventh November, 1651, in EVELYN'S *Diary**, "He gave me," says Mr. EVELYN, "a certain powder, with which he affirmed that he had fixed mercury before the late king. He advised me to try and digest a little better, and gave me a water which he said was only rain water, of the autumnal equinox, exceedingly rectified and very volatile: it had a taste of strong vitriolic, and smelt like aquafortis. He intended it for a dissolvent of calx of gold; but the truth is, Sir KENELM was an arrant mountebank."

The following is another history of transmutation, given by Mangetus (Preface to the *Bibliotheca Chemica Curiosa*), on the authority of M. Gros, a clergyman of Geneva, "of the most unexceptionable character, and at the same time a skilful physician and expert chemist."

"About the year 1650 an unknown Italian came to Geneva, and took lodgings at the sign of the *Green Cross*. After remaining there a day or two, he requested De Luc, the landlord, to procure him a man acquainted with Italian, to accompany him through the town and point out those things which deserved to be examined. De Luc was acquainted with M. Gros, at that time about twenty years of age, and a student in Geneva, and knowing his proficiency in the Italian language, requested him to accompany the stranger. To this proposition he willingly acceded, and attended the Italian everywhere for the space of a fortnight. The stranger now began to complain of want of money, which alarmed M. Gros not a little, for at that time he was very poor, and he became apprehensive, from the tenour of the stranger's conversation, that he intended to ask the loan of money from him. But instead of this, the Italian asked him if he was acquainted with any goldsmith, whose bellows and other utensils they might be permitted to use, and who would not refuse to supply them with the different articles requisite for a particular process which he wanted to perform. M. Gros named a M. Bureau, to whom the Italian immediately repaired. He readily furnished crucibles, pure tin, quicksilver, and the other things required by the Italian. The goldsmith left his workshop, that the Italian might be under the less restraint, leaving M. Gros, with one of his own workmen, as an attendant. The Italian put a quantity of tin into one crucible, and a quantity of quicksilver into another. The tin was melted in the fire, and the mercury heated. It was then poured into the melted tin, and at the same time a red powder enclosed in wax was projected into the amalgam. An agita-

* BRAY'S *Memoirs of John Evelyn*.

tion took place, and a great deal of smoke was exhaled from the crucible; but this speedily subsided, and the whole being poured out, formed six heavy ingots, having the colour of gold. The goldsmith was called in by the Italian, and requested to make a rigid examination of the smallest of these ingots. The goldsmith not content with the touchstone and the application of aquafortis, exposed the metal on the cupel with lead, and fused it with antimony, but it sustained no loss. He found it possessed of the ductility and specific gravity of gold; and full of admiration, he exclaimed that he had never worked before upon gold so perfectly pure. The Italian made him a present of the smallest ingot as a recompense, and then, accompanied by M. Gros, he repaired to the Mint, where he received from M. Bacuet, the mint-master, a quantity of Spanish gold coin, equal in weight to the ingots which he had brought. To M. Gros he made a present of twenty pieces, on account of the attention that he had paid to him; and, after paying his bill at the inn, he added fifteen pieces more, to serve to entertain M. Gros and M. Bureau for some days, and in the mean time he ordered a supper, that he might, on his return, have the pleasure of supping with these two gentlemen. He went out, but never returned, leaving behind him the greatest regret and admiration. It is needless to add, that M. Gros and M. Bureau continued to enjoy themselves at the inn till the fifteen pieces, which the stranger had left, were exhausted."

Many of the alchemists have given in detail the processes for the preparation of the Philosopher's Stone; but they are all unsatisfactory, and many of them unintelligible*. The following, which is one of the plainest, is offered as a sample of the general tenour of their proceedings; it is the formula of Carolus Musitanus†.

"1. Prepare a quantity of spirit of wine, so free from water that it is wholly combustible, and so volatile that when a drop of it is let fall it evaporates before it reaches the ground; this constitutes the first menstruum.

"2. Take pure mercury, revived in the usual manner from cinnabar; put it into a glass vessel with common salt and distilled vinegar; agitate violently, and when the vinegar acquires a black colour, pour it off and add new vinegar; agitate again, and continue these repeated agitations and additions till the vinegar ceases to acquire a black colour from the mercury: the mercury is now quite pure and very brilliant.

"3. Take of this mercury four parts; of sublimed mercury‡ (*mercurii meleorisati*), prepared with your own hands, eight parts; triturate them together in a wooden mortar with a wooden pestle, till all the grains of running mercury disappear. This process is tedious and rather difficult.

"4. The mixture thus prepared is to be put into an aludel, or a sand-bath, and exposed to a subliming heat, which is to be gradually raised till the whole sublimes. Collect the sublimed matter, put it again into the aludel, and sublime a second time; this process must be repeated five times. Thus a very sweet and crystallized sublimate is obtained: it constitutes the salt of wise men (*sal sapientum*), and possesses wonderful properties§.

* See STAHL's *Fundamenta Chemicæ*,
and JUNKER's *Conspectus Chemicæ*.

† MANGETI *Bibliotheca Chémica*.

‡ Probably corrosive sublimate.

§ Probably calomel.

"5. Grind it in a wooden mortar, and reduce it to powder; put it into a glass retort, and pour upon it the spirit of wine (No. 1) till it stands about three finger-breadths above the powder; seal the retort hermetically, and expose it to a very gentle heat for seventy-four hours, shaking it several times a-day; then distil with a gentle heat and the spirit of wine will pass over, together with spirit of mercury. Keep this liquid in a well-stopped bottle, lest it should evaporate. More spirit of wine is to be poured upon the residual salt, and after digestion it must be distilled off as before; and this process must be repeated till the whole salt is dissolved, and distilled over with the spirit of wine. You have now performed a great work. The mercury is now rendered in some measure volatile, and it will gradually become fit to receive the tincture of gold and silver. Now return thanks to God, who has hitherto crowned your wonderful work with success; nor is this great work involved in Cimmerian darkness, but clearer than the sun; though preceding writers have imposed upon us with parables, hieroglyphics, fables, and enigmas.

"6. Take this mercurial spirit, which contains our magical steel in its belly, put it into a glass retort, to which a receiver must be well and carefully luted: draw off the spirit by a very gentle heat, there will remain in the bottom of the retort the quintessence or soul of mercury; this is to be sublimed by applying a stronger heat to the retort that it may become volatile, as all the philosophers express themselves,

Si fixum solvas faciesque volare solutum,
Et volucrum figas faciet te vivere tutum.¹

This is our luna, our fountain, in which the king and queen may bathe. Preserve this precious quintessence of mercury, which is very volatile, in a well-shut vessel for further use.

"7. Let us now proceed to the operation of common gold, which we shall communicate clearly and distinctly, without digression or obscurity; that from vulgar gold we may obtain our philosophical gold, just as from common mercury we obtained, by the preceding processes, philosophical mercury.

"In the name of God, then, take common gold, purified in the usual way by antimony, convert it into small grains, which must be washed with salt and vinegar, till it be quite pure. Take one part of this gold, and pour on it three parts of the quintessence of mercury; as philosophers reckon from seven to ten, so we also reckon our number as philosophical, and we begin with three and one; let them be married together like husband and wife, to produce children of their own kind, and you will see the common gold sink and plainly dissolve. Now the marriage is consummated; now two things are converted into one: thus the philosophical sulphur is at hand, as the philosophers say, *the sulphur being dissolved, the stone is at hand*. Take then, in the name of God, our philosophical vessel, in which the king and queen embrace each other as in a bedchamber, and leave it till the water is converted into earth, then peace is concluded between the water and fire, then the elements have no longer anything contrary to each other; because, when the elements are converted into earth they no longer oppose each other; for in earth

all elements are at rest. For the philosophers say, 'When you shall have seen the water coagulate itself, think that your knowledge is true, and that your operations are truly philosophical.' The gold is now no longer common, but ours is philosophical, on account of our processes: at first exceedingly fixed, then exceedingly volatile, and finally exceedingly fixed; and the whole science depends upon the change of the elements. The gold at first was a metal, now it is a sulphur, capable of converting all metals into its own sulphur. Now our tincture is wholly converted into sulphur, which possesses the energy of curing all diseases: this is our universal medicine against all the most deplorable diseases of the human body; therefore, return infinite thanks to Almighty God for all the good things which he has bestowed upon us.

"In this great work of ours, two modes of fermenting and projecting are wanting, without which the uninitiated will not easily follow our process. The mode of fermenting is as follows:—Take of our sulphur above described one part, and project it upon three parts of very pure gold fused in a furnace; in a moment you will see the gold, by the force of the sulphur, converted into a red sulphur of an inferior quality to the first sulphur: take one part of this, and project it upon three parts of fused gold, the whole will be again converted into a sulphur, or a friable mass; mixing one part of this with three parts of gold, you will have a malleable and extensible metal. If you find it so, well; if not, add other sulphur, and it will again pass into sulphur. Now the sulphur will be sufficiently fermented, or our medicine will be brought into a metallic nature.

"The mode of projecting is this:—Take of the fermented sulphur one part, and project it upon ten parts of mercury, heated in a crucible, and you will have a perfect metal; if its colour is not sufficiently deep, fuse it again, and add more fermented sulphur, and thus it will acquire colour. If it becomes frangible, add a sufficient quantity of mercury and it will be perfect.

"Thus, friend, you have a description of the universal medicine, not only for curing diseases and prolonging life, but also for transmuting all metals into gold. Give therefore thanks to Almighty God, who, taking pity on human calamities, has at last revealed this inestimable treasure, and made it known for the common benefit of all."

Nearly all the alchemists attributed the power of prolonging life, either to the philosopher's stone, or to certain preparations of gold, imagining possibly that the permanence of that metal might be transferred to the human system. The celebrated DESCARTES is said to have supported such opinions; he told Sir KENELM DIGBY, that although he would not venture to promise immortality, he was certain that life might be lengthened to the period of that of the Patriarchs. His plan, however, seems to have been the very rational one of limiting all excess of diet, and enjoining punctual and frugal meals*.

The history of alchemy has been greatly enriched by the labours of the celebrated ELIAS ASHMOLE, who in 1652 published his *Theatrum Chemicum Britannicum*, containing several Poetical Pieces of our famous

* See *Life of Descartes*, CHALMERS'S *Biographical Dictionary*.

English Philosophers, who have written the Hermetique Mysteries in their owne ancient Language.

The most remarkable piece in this collection is the *Ordinall of Alchimy*, by THOMAS NORTON, illustrated by several curious cuts. It treats, in separate chapters, of the objects of the occult science; of the difficulties of attaining them; of the different methods of pursuing them; of the characters of the elements; and of the five concords, of which the first is *Patience*, the second *Assistance*, the third *Instruments*, the fourth *Situation*, and the fifth *Planetary Influence*. It is difficult to select from this production any specimen capable of conveying an idea of its merits, that can come within the limits of a quotation. Perhaps the following lines, picked out of the seventh chapter, touching "the Regiment of Fiers," may serve to convey some idea of the author's talents in the double capacity of poet and philosopher:—

In many authors written you may see,
Totum consistit in ignis regimine;
 Wherefore in all things so proceed,
 That heat work no more no less than it need;
 Wherein many of Geber's cooks
 Deceived were, though they be wise in books.
 Such heate wherewith a pig or goose is scalded
 In this arte *Decoction* it is called;
 Such heate as dryeth lawne karchiefs fair,
 In thirty operations serveth for our ayre!
 But for divisions you must use such heate,
 As cook's make when they roaste raw meate.
Ignis humidus another fier alsoe
 Is, and yet seemeth *oppositum in adjecto*:
 Another fier is fier of desication,
 For matters which be imbibed with humectation.
Ignis corrodens serveth in this arte,
Elementa propinqua wisely to depart.
 By one point of excess all your work is shent,
 And one point too little is insufficient;
 Who can be sure to find its true degree,
Magister magnus in igne shall he be.
 All that hath pleasure in this booke to reade,
 Pray for my soule, and all both quick and deade.
 In this year of Christ 1477,
 This work was began, honour to God in heaven.

In later times we have had two or three believers in transmutation. In the year 1782, Dr. PRICE of Guildford, by means of a white and red powder, professed to convert mercury into silver and gold, and is said to have convinced many disbelievers of the possibility of such change; his experiments were to have been repeated before an adequate tribunal, but he put a period to his existence by swallowing laurel-water.

Another true believer in the mysteries of this art was PETER WOULFE, of whom it is to be regretted that no biographical memoir has been preserved. I have picked up a few anecdotes respecting him from two or three friends who were his acquaintance. He occupied chambers in Barnard's Inn, while residing in London, and usually spent the summer in Paris. His rooms, which were extensive, were so filled with furnaces and apparatus that it was difficult to reach his fire-side. Dr. Babington told me, that he once put down his hat, and never could find it again, such was

the confusion of boxes, packages, and parcels, that lay about the chamber. His breakfast hour was four in the morning; a few of his select friends were occasionally invited to this repast, to whom a secret signal was given by which they gained entrance, knocking a certain number of times at the inner door of his apartment. He had long vainly searched for the elixir, and attributed his repeated failures to the want of due preparation by pious and charitable acts. I understand that some of his apparatus is still extant, upon which are supplications for success, and for the welfare of the adepts. Whenever he wished to break an acquaintance, or felt himself offended, he resented the supposed injury by sending a present to the offender, and never seeing him afterwards. These presents were sometimes of a curious description, and consisted usually of some expensive chemical product or preparation. He had an heroic remedy for illness: when he felt himself seriously indisposed, he took a place in the Edinburgh mail, and, having reached that city, immediately came back in the returning coach to London. A cold, taken on one of these expeditions, terminated in an inflammation of the lungs, of which he died in 1805. He is the author of several papers in the *Philosophical Transactions*. Several pieces of his apparatus, and, among others, an *athanor*, or self-supplying furnace, were given me by Mr. HATCHETT, who purchased them of Mr. Woulfe: they are in the Laboratory of the Royal Institution.

A few other persons of less note might be quoted as believers in transmutation, but the history of one is that of all; and, in the emphatic language of Spenser, they were doomed

To lose good days that might be better spent,
To waste long nights in pensive discontent;
To speed to-day, to be put back to-morrow,
To feed on hope, to pine with fear and sorrow;
To fret their souls with crosses and with cares,
To eat their hearts through comfortless despairs:
Unhappy wights! born to disastrous end,
That do their lives in tedious tendance spend.

But although the alchemists have given us little in the way of useful facts or applicable discoveries, their reign was fruitful in the invention of apparatus. Alembics, stills, retorts, receivers, and a variety of whimsical and complex vessels, in glass and porcelain, are described and depicted in their works; and they not only possessed nearly all the furnaces with which our modern laboratories are necessarily supplied, but were particularly expert in their construction.

§ III.

THERE are many points in alchemical history which have been purposely passed over, as affording nothing worthy of remark, and as suggesting nothing that throws light upon the brighter ages of chemistry. It has been too common to load the alchemists with honours which they ill deserve: the picture of their proceedings, already given, is as correct and faithful as the materials that compose it admit of, and it presents little that the mind rests upon with satisfaction, or reverts to with interest or profit. But there were contemporaries with the alchemists, whose pursuits were conducted upon more rational principles, and whose writings,

though often overshadowed by the clouds of magic and astrology, are, in many instances, illumined by rays of sober experimental investigation: they often indulge in the insane caprices of the mere searchers for the philosopher's stone, but their madness has method in it, and their wanderings are not without a plan.

Of these, the first I shall notice, is BASIL VALENTINE* of Erfurth, who wrote about the middle of the fifteenth century, and who may justly be considered as one of those whose labours contributed to the foundation of modern chemistry: his experiments always had an object, and he details them with intelligible perspicuity. It is true that he often launches into alchemy, but he returns unpolluted by its follies: where he speaks as an adept he is as absurd as need be; but, as the narrator of experiments, he abounds in shrewd remarks, and was uncommonly successful in his pursuits. The extant works of BASIL VALENTINE are not numerous, and they have mostly become scarce. In 1671 his *Triumphal Chariot of Antimony* was republished at Amsterdam, from the original edition of 1624, with copious notes by Dr. THEODORE KIRKCRINGIUS; and a few years after an English translation of that celebrated production was printed at London. In 1644 his *Haliographia* appeared at Bologna. This work treats of the preparation, uses, and virtues of mineral, animal, and vegetable salts, and is a curious and well-digested body of information upon a variety of chemical subjects. These are the only works of BASIL VALENTINE that I have been able to meet with, and I believe they contain the pith of his chemical knowledge. In both these works he appears in the double capacity of chemist and physician. In physic he was a brave champion for the chemical sect, and his *Triumphal Chariot of Antimony*, especially, abounds in reflections, not of the mildest description, upon the practice and theories of his adversaries, whom he despises, because, unable to prepare their own medicines, "they know not whether they be hot or cold; moist or dry; black or white; they only know them as written in their books, and seek after nothing but money. Labour is tedious to them, and they commit all to chance; they have no conscience; and coals are outlandish wares with them; they write long scrolls of prescriptions, and the apothecary thumps their medicine in his mortar, and health out of the patient."

But when we find many most important facts recorded in the pages of this writer, we shall readily excuse the irrelevant matter by which they are accompanied; and, in this view, his writings deserve the attentive perusal of those who would trace modern improvements to their parent inventions and discoveries, and these to their more remote and recondite sources. To say nothing of the important preparations of antimony with which BASIL VALENTINE enriched the *Materia Medica*, and of which he has given an intelligible and copious account in the *Currus Triumphalis*, we find in his works the first accurate directions for the preparation of nitric, hydrochloric, and sulphuric acids; and were these his only contributions to the laboratory, I need hardly say how richly he merits the eulogies of the moderns, when we reflect upon the numerous uses to which those acids are now applied, upon their importance in several of the most refined and extensive branches of art, and upon the ad-

* Born about the year 1400.

vances in technical and scientific chemistry which have been attained by their aid.

In order to obtain the *water of nitre*, for by that name he designates the acid, VALENTINE directs us to distil three parts of powdered earthenware with one of nitre. The mixture is to be subjected in a proper earthen alembic to a red heat, and a capacious receiver annexed. Now, this process is, in some places, still practised, and, although neither convenient, nor, generally speaking, economical, the acid it affords is sufficiently pure. The opinion of the old chemists, respecting this production of nitric acid, was, that the clay held down the nitre so as to expose it to the searching influence of the fire; but the decomposition depends upon the attraction of the potassa of the nitre for the ingredients of the clay, a kind of red slag remaining in the retort.

Another mode of procuring nitric acid mentioned by this writer, though probably of more ancient date, since RAYMOND LULLY seems to have known it, comes nearer to the process now in common use, and may, in many situations, be conveniently and economically practised. It consists in distilling equal parts of nitre and green vitriol. The residue consists of sulphate of potassa and oxide of iron; the former may be separated by washing with hot water, and an oxide of iron, of a deep red colour remains, used by the polishers of plate-glass, under the name of *colcothar*.

Under the directions for preparing the salt of gold in the *Haliographia*, I find a third mode suggested for the production of acid from nitre, which consists in distilling saltpetre with finely-pounded flints. It depends upon the attraction of silica for potassa, which combine to form a glassy slag, or silicate of potassa.

Such are the facts which are recorded by BASIL VALENTINE respecting the preparation of nitric acid; he termed it *water*, or *acid spirit* of nitre. It was afterwards called *aquafortis*; and its property of dissolving gold, with the addition of sal ammoniac, or of hydrochloric acid, is often adverted to and descanted upon by the same author.

For nearly two hundred years after the discovery of *aquafortis*, its chemical history was but little advanced; nor, indeed, were any facts of importance respecting its true nature made out, until Dr. PRIESTLEY and Mr. CAVENDISH commenced their researches, about the middle of the last century.

But the discovery of nitric acid is certainly second in importance to that of oil of vitriol, or, as it is now called, *sulphuric acid*, the honour of which is also due to BASIL VALENTINE; for it is not, as far as my information goes, described in any earlier writer: he frequently mentions it, and the mode of its preparation; and PARACELUSUS, and the authors who immediately followed, talk of it as well known, and in common use, though it is probable that it bore a higher price, and was but scantily supplied.

In the *Currus Triumphalis*, the spirit afforded by the distillation of vitriol is not unfrequently adverted to, and its action upon certain antimonial compounds so fully described, as to leave no doubt respecting its nature. In the *Haliographia*, however, *oil of vitriol* is distinctly mentioned; and, what is curious, we find in the chapter of that tract relating to the extraction of the salts of iron, particular directions for the prepara-

tion of sulphate of iron, by dissolving iron filings in a mixture of one part of oil of vitriol and two of water: this solution, he says, "when put aside in a cool place, soon forms beautiful crystals;" and in another section we are told, that "this salt is an excellent tonic; that it comforts weak stomachs; and that, externally applied, it is an admirable styptic." And this, in fact, is nearly all that we can say of the preparation and medical uses of this salt of iron at the present day.

The mode of obtaining sulphuric acid, by the distillation of sulphate of iron, or green vitriol, is still extensively practised upon the Continent, in Germany, Sweden, and more especially at Bleyl, in Bohemia*. The vitriol is first deprived of water of crystallization, and then submitted, in glass retorts coated with clay, to a red heat; white fumes pass over into the receivers, which become very hot during the condensation of these fumes into an unctuous reddish-brown fluid, which, from its viscosity and appearance, acquired the name of *oil of vitriol*: there remains in the vessels a substance of a fine red colour, which, when washed and levigated, furnishes the *colcothar*, or *caput mortuum* of vitriol; for the old chemists were in the habit of representing the dregs and last products of substances by the symbol of a death's head and cross-bones.

The oil of vitriol, thus prepared, exhales fumes when exposed to a moist atmosphere, and occasionally congeals or crystallizes; circumstances which led to its name of *glacial oil of vitriol*, and which show that it differs from the acid as ordinarily prepared. It contains, in fact, the anhydrous acid.

That sulphur, during combustion, produces a portion of acid matter, seems to have been known at a very early period; the method of obtaining sulphuric acid by burning a mixture of sulphur and nitre is described by VALENTINE in his *Chariot of Antimony*, under the name of *oil of antimony*, for he employed sulphuret of antimony, as well as sulphur, in its production. The original recipe runs thus:—

"Take of antimony, sulphur, salt nitre, of each equal parts, fulminate them under a bell, as oil of sulphur, *per campanam*, is made, which way of preparing hath long since been known to the ancients; but you will have a better way if instead of a bell you take an alembic, and apply to it a recipient; so you will obtain more oil, which will indeed be of the same colour as that made of common sulphur, but in powers and virtues not a little more excellent."

Dr. WARD, the inventor of many celebrated nostrums, was the first person who brought this mode of preparing sulphuric acid into notice in England; he obtained a patent for his invention, and for a considerable time monopolized the manufacture. At length Dr. ROEBUCK, an eminent physician of Birmingham, substituted an apparatus of lead for the glass vessels previously used. This was in 1746, since which the price of sulphuric acid has been greatly reduced, and the manufacturer consequently enabled to employ it for a variety of purposes, to which it was previously inapplicable, from its scarcity and high price. In 1772, the first manufactory of sulphuric acid near the metropolis was established by Messrs. KINGSCOTE and WALKER, at Battersea†.

* AIKIN'S *Dictionary*, art. Sulphuric Acid. † PARKES' *Chemical Essays*, vol. ii., p. 388.

I have mentioned that the necessity and advantages of nitre, as an addition to sulphur in increasing the acid product, was known to VALENTINE; but the manner in which it operates is a later discovery. As the expense of the operation is increased by it, many attempts have been made to supersede its use, by the employment of other materials, under the impression that it merely furnished oxygen; but a little reflection easily proves the fallacy of such a notion; for, even if we burn sulphur in pure oxygen, sulphurous, and not sulphuric acid, is the result. The solution of this chemical problem has been chiefly effected by the researches of M.M. CLEMENT and DESORMES, and Sir H. DAVY, who have proved that the products of the nitre are concerned in transferring oxygen to the sulphur. A patent has more lately been taken out for a mode of preparing sulphuric acid by the combustion of pyrites, without the intervention of nitre, but its success is doubtful.

The numerous antimonial preparations described in the *Chariot of Antimony* deserve more notice than they have generally received from the chemical historian; and the perusal of that work affords some insight into the celebrated disputes between the galenical and chemical physicians, which were afterwards pushed so far by PARACELSUS.

BASIL VALENTINE, adverting to the notion that antimony* was poisonous, tells us, that its noxious qualities may not only be subdued by art, but that various properties may be communicated to its different preparations—"As a blacksmith," he says, "with one sort of fire, and iron only is his matter, of which he forms divers instruments. Sometimes he makes a spit, at another time horse-shoes, another time a saw, and at length innumerable other things, every of which serves for that use for which the smith intended it. So of antimony various works may be made for different uses; in which the artist is the smith that forms, Vulcan is the key which opens, and operation and utility give experience and knowledge of the use. Oh, if foolish and vain men would hear and understand what I write, they would not suck their turbid and insalubrious potions, but hasten to these limpid fountains, and drink of the well of life."

In pursuing his defence of antimony, the author allows its venomous nature, but then tells us, that upon that circumstance its value in medicine depends, upon the principle that venom draws venom to itself; and adduces, as proof of this position, the well-known fact, as he terms it, that a dried toad reduced to powder, and sprinkled upon the wound occasioned by a viper's bite, cures it.

§ IV.

PARACELSUS comes next in chronological order to his predecessor, BASIL VALENTINE, but as a chemist he falls far short of that master; his original

* It is probable that the word *Antimony* was first used by Basil Valentine. Tradition relates that having thrown some of it to the hogs, after it had purged them heartily, they immediately fattened; and, therefore, he imagined

that his fellow monks would be the better for a like dose, they having become lean by fasting and mortification. The experiment, however, failed, and they died; whence the medicine was called *Antimoine*.

discoveries are few and unimportant, and his great merit lies in the boldness and assiduity which he displayed in introducing chemical preparations into the *Materia Medica*, and in subduing the prejudices of the galenical physicians against the productions of the laboratory. The principal events of his life are the following: His real name was PHILIP HOCHENER, which he changed, on commencing his professional career, into THEOPHRASTUS BOMBASTUS PARACELUS*. At an early age he visited the most renowned towns in Europe, and, returning to his native country, was made Professor of Medicine and Chemistry at Basle; he availed himself of this public situation, not to instruct the unlearned, but to vilify his contemporaries and predecessors. It is generally said, that his dissolute manners and intractable temper obliged him to quit his occupation. But others have told a more plausible story: a rich Canon fell sick, and getting frightened, offered a hundred florins to any one who would cure him. PARACELUS administered three pills, and the Canon got well; but being so soon restored, and by such simple means, he refused to fulfil his promise. The matter was brought before a magistrate, who decreed that the doctor should only recover the customary fee. Irritated at the flimsy excuses and unpardonable ingratitude of the priest, and at the magistrate's partial decision, PARACELUS declared that he would leave the inhabitants of Basle to the eternal destruction which they deserved: he then retired to Strasburgh, and thence into Hungary, where he took to drinking, and died in great poverty at Salzburgh, in 1541, and in the forty-third year of his age. Though we can fix upon no particular discovery on which to found his merits as a chemist, and though his writings are deficient in the acumen and knowledge displayed by several of his contemporaries and immediate successors, especially by THEODORE DE MAYERNE, and DU CHESNE, or, as he was generally called, QUERCITANUS†, it is undeniable that he gave a most important turn to pharmaceutical chemistry; and calomel, first described by CROLLIUS‡ in 1609, with a variety of mercurial and antimonial preparations, as likewise opium, came into general use. Although the chemical physicians, however, were very successful, they were aware of the unpopularity of their means; people were frightened at the idea of mercury and antimony,

* "Hunc virum," says Boerhaave, "alii coluerunt pro Deo, imo locutus sum cum hominibus qui credunt eum non esse mortuum, sed vivum sedere in sepulchro pertæsum peccatorum et malorum hominum." The following is an illustrative anecdote of his impudence: "Cum adscenderet Cathedram physico-medicam, sumsit vas æneum cum igne, immisit sulphur et nitrum, et simul Galenum, Avicennam, et Arabes conjecit in ignem, dicens, sic vos ardebitis in gehennâ."

† Du Chesne was a native of Gascony, and physician to Henry the Fourth.

‡ Oswald Crollius was physician to the Prince of Anhalt, and a counsellor of the Emperor Rodolph the Second. His practice and system were opposed

by the celebrated Andrew Libavius, of Halle, who died in 1616. His works were published in 1615, at Frankfort, in 3 vols., folio. Libavius was succeeded by Angelus Sala, of Vicenza, physician to the Duke of Mecklenburgh Schwerin, whose works were published at Frankfort, in 1647, in 1 vol., 4to. The perusal of these authors will be interesting to those who are studying the history of medicine, on account of the important additions which they made to Chemical Pharmacy, and the new substances with which they enriched the *Materia Medica*. They were followers of the doctrines of Paracelsus, but divested their practice of the absurdities in which his tenets were involved.

which were accordingly exhibited under fantastic and assumed names. Towards the end of the fifteenth century, the use of antimony was prohibited at Paris; and BESNIER was expelled the faculty for having persevered in administering it. In England, chemical medicines first began to be extensively employed in the reign of Charles the First. In 1644 SCHRÖDER published his *Chemico-Medical Pharmacopœia*; and shortly after, that of the London College made its appearance; but although the history of pharmaceutical chemistry must not be blended with the abstract progress of the science, yet should it not be forgotten, that the great modern improvements in chemistry have sprung from its applications to medicine, and that the foundations of chemical science are to be found in the medical and pharmaceutical writers of the sixteenth century, who rescued it from the hands of the alchemical pretenders, and gave it a place and character of its own.

The enthusiastic ravings of PARACELSUS tended to awaken the more solid talents of VAN HELMONT of Brussels, who flourished in the early part of the seventeenth century, and who studied and admired the works of his less modest predecessor. VAN HELMONT has left a curious memoir, containing a sketch of his own life, and exhibiting the various circumstances that gave an impulse to his proceedings, and the different causes that suggested his pursuits. In this biographical relic, there is a vein of sound and unaffected argument, which displays a very amiable turn of mind in the writer. It would, however, be irrelevant to my present subject to give more than a brief abstract, illustrative of the style and pursuits of the author:—"In 1594, being then seventeen years of age, I finished my course of philosophy; but upon seeing none admitted to examinations at Louvain who were not in a gown and hood, as though the garment made the man, I was struck with the mockery of taking degrees in arts. I therefore thought it more profitable seriously and conscientiously to examine myself; and then I perceived that I really knew nothing, or, at least, nothing that was worth knowing. I had, in fact, merely learned to talk and to wrangle, and therefore refused the title of Master of Arts, finding that nothing was sound, nothing true, and unwilling to be declared master of the seven arts, when my conscience told me I knew not one. The Jesuits, who then taught philosophy at Louvain, expounded to me the disquisitions and secrets of magic; but these were empty and unprofitable conceits; and, instead of grain, I reaped stubble. In moral philosophy, when I expected to grasp the quintessence of truth, the empty and swollen bubble snapped in my hands. I then turned my thoughts to medicine, and having seriously read GALEN and HIPPOCRATES, noted all that seemed certain and incontrovertible; but was dismayed upon revising my notes, when I found that the pains I had bestowed, and the years I had spent, were altogether fruitless; but I learned at least the emptiness of books and formal discourses and promises of the schools. I went abroad, and there I found the same sluggishness in study, the same blind obedience to the doctrines of their forefathers, the same deep-rooted ignorance*."

* *Johannis Baptistæ Van Helmont* | extract is from the *Studia Authoris*,
Opera omnia. Hafn. 1707. The above | p. 16.

VAN HELMONT was called by his contemporaries an insane enthusiast; but there is, even in the imperfectly translated and brief quotation which I have taken from the history of his studies, a propitious gleam of that dawn of improvement which was diffused over science by the genius of Lord BACON.

The doctrine of the Chemical Elements was in full vogue during the time of VAN HELMONT, PARACELSUS, and VALENTINE, and salt, sulphur, and mercury, are unequivocally mentioned as the ultimate component parts of almost all the forms of matter. In the writings of VAN HELMONT, there are sundry allusions to the existence of æriform bodies, and the word *gas*; now in common use, and applied to all æriform matters differing from atmospheric air, first occurs in his pages: he also distinguishes between condensable gases or vapours, and incondensable or permanently elastic fluids; and under the term *gas silvestre*, he seems to comprehend what was afterwards called *fixed air*. As to the general tenour of his writings, it is difficult to separate the chemistry from the miscellaneous matters, and more especially from the medical commentaries with which it is blended; but they abound in hints and observations, which are ingenious and acute. In his experiments on air, he argued very plausibly on its weight and elasticity; and has detailed with much precision the effect of temperature and pressure, in his description of the air thermometer.

Entering upon the seventeenth century, the historian of Experimental Science must ever pause to pay a tribute of gratitude and respect to the celebrated FRANCIS BACON; a man whose faults as a statesman have been eclipsed to the eyes of posterity by the brilliancy and excellence of his philosophical character.

It may usually be observed, that those who are gifted by nature with superior genius or uncommon capacity, who are destined to reach the meridian of science, or to attain exalted stations in the learned professions, have exhibited early symptoms of future greatness: either indefatigable industry, or extraordinary sagacity, or ardent enthusiasm, have marked their entrance into the affairs of life. At the age of sixteen, BACON was distinguished at Cambridge; and, very shortly afterwards, struck with the frivolous subtilty of the tenets of ARISTOTLE, he appears to have turned his mind into that channel which led on to future eminence. The solid foundation of his scientific character is the *Instauration of the Sciences*. It opens with a general and philosophical survey of the subject; whence he proceeds to infer the futility of the ancient philosophical systems, and to point out Induction, from sober and severe experiment, as the only road to truth. Pursue this, he says, and we shall obtain new powers over nature; we shall perform works as much greater than were supposed practicable by natural magic, as the real actions of a Cæsar surpass the fictitious ones of a hero of romance. Speculative Philosophy he likens to the lark, who brings no returns from his elevated flight; Experimental Philosophy to the falcon, who soars as high, and returns the possessor of his prey. Illustrations of the new method of philosophizing, and the mode of arranging results, conclude this admirable and unrivalled performance.

To do justice to this work, we must, for a moment, forget the present

healthy and vigorous constitution of science, and view it deformed and sickly in the reign of ELIZABETH. We shall then not be surprised at the irrelative observations and credulous details which occasionally blemish this masterly production of the human mind.

But the history of LORD BACON furnishes other materials for reflection. Upon the accession of JAMES THE FIRST, he became successively possessed of the highest honours of the law, and acquired great celebrity as a public speaker and a man of business; yet, amidst the harassing duties of his laborious avocations, he still found time to cultivate and adorn the paths of science, the pursuit of which furnished employment for his scanty leisure and relaxation in his professional toils; and, when ultimately disgraced, "his genius, yet unbroken, supported itself amidst involved circumstances and a depressed spirit, and shone out in literary productions." Nor should the munificence of his royal master remain unmentioned, who, after remitting his fine, and releasing him from his prison in the Tower, conferred upon him a large pension, and used every expedient to alleviate the burden of his age, and to blunt the poignancy of his sufferings.

After the death of LORD BACON, which happened in April, 1626, in the sixty-sixth year of his age, the records of science begin to assume a brighter aspect; and we discern true knowledge emerging from the dungeons of scholastic controversy, and shaking off the chains of polemical learning.

The middle of the seventeenth century was a period extremely fertile in chemical productions. In taking, however, a comprehensive view of the writers of this age, there are a few only whose labours deserve to be recorded as connected with the advancement of chemical knowledge; that is, as having contributed, by new views and discoveries, to the progress of what may be termed the philosophy of the science. They were generally mere recorders of insulated facts, or publishers of ill-digested and imperfectly-arranged catalogues of the various preparations that were used in the arts and in medicine; for the dread in which chemical preparations were viewed by physicians began now to decline; the *Materia Medica* was filled with new and more convenient forms, and the *Pharmacopœiæ*, published under the authority of different governments, were allowed to divulge the preparation of calomel, emetic tartar, and several other important and useful compounds.

Among the writers of this period there is no one more rich in facts, and original in invention, than GLAUBER of Amsterdam. KUNCKEL was a successful promoter of chemistry applied to the arts: he wrote on the production of phosphorus, and on the art of glass-making, and was a favourite at many courts of Europe, more especially with CHARLES THE ELEVENTH of Sweden, who, in 1693, granted him letters of nobility. In 1673, LEMERY, the elder, conferred much service on chemistry by his dexterity as an experimentalist, and by the plain, perspicuous style in which he publicly taught the rudiments of the science. The discovery of phosphorus belongs also to this period; and, although of little interest perhaps in the abstract, it drew a host of inquirers into the precincts of the laboratory, and was productive of more extensive and important consequences than have generally been attributed to it.

Of these writers, there is no one so deserving attention as GLAUBER: he was not a mere maker of experiments, but he reasoned sensibly and even acutely upon their results; he occasionally oversteps the bounds of modest argument, rudely deprecates the views of his contemporaries, and praises himself beyond all measure; but this vitiated style was then in fashion, and, unlike most of his contemporaries, he has very sufficient claims to originality of invention. His works were translated into English, and published, as the title runs, "for public good, by the labour, care, and charge of CHRISTOPHER PACKE, *Phylo-Chemico-Medicus*, in 1689."

GLAUBER was so laborious an experimentalist, and in his experiments there is so much originality, that it is difficult to select those which can strictly be called discoveries, and upon which his scientific character deserves chiefly to be founded.

The distillation of volatile alkali from bones, and its conversion into sal ammoniac by the affusion of spirit of salt; the preparation of sulphate of ammonia, which he calls *secret sal ammoniac*, and its conversion into common sal ammoniac by distillation with common salt; the production of blue vitriol by the action of acid of vitriol upon the green rust of copper; the distillation of vinegar from wood, and the formation of a variety of salts useful in medicine and the arts by its action upon alkaline, earthy, and metallic substances; the distillation of muriatic acid, or spirit of salt, from a mixture of common salt and acid of vitriol; and the extraction of sulphate of soda, or *sal mirabile*, from the residue of this experiment, are a few, and only a very few, of the truly important inventions and discoveries that crowd upon us in the perusal of the verbose pages of GLAUBER. Of these the production of vinegar of wood, and of muriatic acid, may perhaps be regarded as of the greatest interest. The acid liquor produced during the destructive distillation of wood has lately become a manufacture of much importance.

GLAUBER describes the distillatory apparatus, which he calls "a press for extracting the juice of wood;" he shows its condensation into an acid liquor; and directs the method of burning lime, by ranging layers of chalk alternately with those of the wood. He also says, that by rectifying the spirit of wood, "a sharp hot oil, of a dark reddish colour remains, and the *vinegar* passes over, fit for the preparation of medicines, and all other uses to which common vinegar is applicable." The oil, he adds, is an admirable preservative of wood, and when saponified with alkali, forms a most valuable manure; "a hogshead of which may be carried into fields and vineyards far remote, more easily than ten loads of common manure, which is carried to vineyards in rocky places with great difficulty. As to the spirit, physicians may use this noble and efficacious juice with great honour and profit in the cure of many diseases hitherto incurable;" and he highly extols the effects of a warm bath, acidulated by the vinegar of wood: he also shows the mode of concentrating it by exposure to cold, when "the phlegm only freezeth, but the sharp spirit remaineth in the middle of the hogshead, so sharp that it corrodeth metals like aqua fortis." After many other shrewd and clever remarks respecting the tar of wood and its acid, GLAUBER closes his discourse, fearing that it will not be believed by many, which, he says, he cannot help; "it contenteth me that I have written the truth, and lighted a candle to my neighbours."

The preparation of muriatic acid, as now commonly conducted, was first devised by GLAUBER; he obtained it by distilling common salt with acid of vitriol, and gives a sufficiently clear account of the nature of the chemical change that ensues. The residue of this operation retains to this day the name of *Glauber's salt*; or, as he termed it, *sal mirabile*. Upon its virtues he has descanted at great length, and though, in his history of this salt, its value and uses are preposterously exaggerated, his observations serve to show the diligence and acuteness with which he investigated its applications, and offer proofs of the extensive information which he possessed relative to many processes of agriculture and the arts. Salt, in short, was GLAUBER's favourite element: "It is," says he, "the beginning and the end of all things, and it increaseth and exalteth their powers and virtues: it is the true universal medicine; not that I would have any man persuade himself, that in these words I would assert immortality, for my purpose tendeth not thither, seeing that I am not ignorant there is no medicine against death." And then, adverting to the opposition to chemical medicines by contemporary physicians, he advises them not to envy those "who have received such divine gifts as his wonderful salt, nor to provoke the innocent with their filthy calumnies and slanders, but to leave those things which exceed their capacities. Nothing," he says, "can extinguish truth; it may be prest, but cannot be overcome; like the sun's light, it may be hidden, but not extinguished."

The directions he gives for the preparation of the *sal mirabile*, and the account of its properties, are in general very correct. "Its colour ought to be white and transparent: its figure is in long striæ or crystals: its taste is like ice melting upon the tongue, and yields some bitterishness. Being dried in the fire, and all the moisture gone off, it will lose about three parts of its own body, and retain a fourth part only; being dissolved in water, it will recover those three parts again. But, on the contrary, if it shoot into a square figure, and hath as yet a saltish taste, and being dried, loseth but little of its weight, it is not worth a rush, and shows that either the oil of vitriol was not good, or not enough of it used in the operation. These things we would not bury in silence, that so we might well advise young beginners, and withdraw them from their errors."

GLAUBER has great merit as an inventor and improver of chemical apparatus, much of which is depicted in the plates attached to his works. The form of distillatory vessels commonly called Woulfe's apparatus, is found in GLAUBER's *Chemical Furnaces*; and he contrived a very ingenious mode of heating large vessels of water by steam, and with great economy of fuel, a method now often resorted to.

He published a pamphlet, entitled *The Consolation of Navigators, in which is taught how they who travel by Sea may preserve themselves from Hunger and Thirst; and also from those Diseases which are wont to happen in long Voyages. Written for the Health, Comfort, and Solace of all those who travel by Water for the good of their Country*. The sensible plan of employing extract of malt as a portable vegetable diet, and dilute muriatic acid to quench thirst, is here recommended; and many of the medicinal uses of the muriatic acid are dwelt upon at length, which have been claimed as recent discoveries. On the whole, there is no author contemporary with GLAUBER, who has written so much to the

purpose, and in whom we find such abundant anticipations of modern scientific improvements. He was cast in the true mould of an experimental chemist, and had he lived in a more propitious age, would probably have rivalled SCHEELE and PRIESTLEY.

§ V.

It is now time to advert to the early proceedings of the Royal Society, as connected with the present subject, a body incorporated by CHARLES THE SECOND in 1662, under a Royal Charter, for the improvement of natural knowledge. The period of the foundation of this Society was peculiarly favourable to its interests and objects; the country, long distracted by the worst of all evils, a civil war, and afterwards oppressed by the military usurpation of CROMWELL, was threatened, upon the death of the Protector, with the horrors of anarchy, when the restoration of CHARLES THE SECOND healed all divisions, and checked the tide of revolutionary violence. Then was a propitious time to lead the rich and well-informed into the avenues of scientific inquiry, and to substitute the advancement of knowledge for political speculation. Among the first members of the Royal Society are the names of many who were eminent in mathematical and physical knowledge, and of more who afterwards became so: they were vehement in favour of experimental science, which was then in its infancy, and soon acquired vigour by their support; and it is curious to observe among the most active and zealous promoters of these peaceful studies, many who had been famed as party leaders, or actively engaged in political intrigues and revolutionary broils.

The early volumes of the *Philosophical Transactions*, of which the first bears date 1665, consist of small numbers, which were published at irregular intervals, and, from their miscellaneous contents, may be compared to the scientific journals of these days. Exclusive of papers read before the Royal Society, they contain many scraps of literary and scientific value collected by the secretary, Mr. OLDENBURGH. The publication was continued by Drs. GREW and HOOKE, but the latter discontinued it, probably from the sparing sale; and in 1683 we find Dr. PLOT resuming the editorship, upon condition that the members would bind themselves to purchase sixty copies of each number. The *Transactions* were periodically published, with some intermissions, however, by the Secretaries of the Society, till the year 1750, when the publication was put into the hands of a Committee of Papers; and since the year 1762 a volume has annually made its appearance*.

In 1666, the Royal Academy of Sciences was instituted at Paris, under the protection of LOUIS THE FOURTEENTH: in its annals the names of HOMBERG, GEOFFROY, and the two LEMERYS, soon became celebrated for their various discoveries and improvements in chemistry. HOMBERG†, under the auspices of the Regent Duke of ORLEANS, was an active and successful experimentalist. He discovered the boracic acid, which he prepared under the name of *sedative salt*. He was also the discoverer of *Pyrophorus*. GEOFFROY deserves mention as an active and scientific con-

* THOMSON'S *History of the Royal Society*.

† Born at Batavia, in Java, 1652; died at Paris, 1715.

tributor to pharmaceutical chemistry; he was also, I believe, the first compiler of the *Paris Pharmacopæia*.

The early proceedings of the Royal Society of London present many traits of the infant state of experimental science, and not a few absurdities might be selected from among them, the principal of which were lampooned by Sir JOHN HILL, in his *Review of the Works of the Royal Society of London*. This period, however, was adorned with the names of BOYLE* and of HOOKE†; the former a voluminous writer, of a most amiable temper and upright mind; the latter, an original and acute experimentalist, but a peevish and distrustful man‡.

Although BOYLE cannot be said to have fathomed the depths of science, yet his station in life, his mild and prepossessing disposition, his strict honour and integrity, and the unaffected earnestness with which he promoted experimental inquiry, tended to shed a lustre on his pursuits, to elevate their character with the world, and to draw into their precincts many who, without such an example, would have passed their lives in that listless inactivity, then too common with those upon whom fortune smiled; among them Mr. BOYLE made many converts. "It must be confessed," says his contemporary EVELYN, "that he had a marvellous sagacity in finding out many useful and noble experiments. Never did stubborn matter come under his inquisition, but he extorted a confession of all that lay in her most intricate recesses, and what he discovered he has faithfully registered and frankly communicated. In this," says EVELYN, "exceeding my Lord VERULAM, who (though never to be mentioned without honour and admiration) was used to tell all that came to hand. His severer studies did not in the least sour his conversation, and I question whether any man has produced more experiments without dogmatising. He was a corpuscularian without Epicurus; a great and happy analyser, addicted to no particular sect, but, as became a generous and free philosopher, preferring truth above all; in a word, a person of that singular candour and worth, that to draw a just character of him, one must run through all the virtues, as well as through all the sciences§."

* Boyle was born in January, 1627, at Lismore, in the Province of Munster, in Ireland. He was educated at Eton, and afterwards travelled in Italy, Switzerland, and France, and returned to England in 1644. In 1668 he took up his residence in London; and in 1680 was elected President of the Royal Society. He died on the 30th of December, 1691, aged sixty-four.

† Born in the Isle of Wight, 1635; died in London, 1702.

‡ Sir Godfrey Copley, in a letter written about the time of Hooke's death, says, "Dr. Hooke is very crazy; much concerned for fear he should outlive his estate. He hath starved one old woman already, and, I believe, he will endanger himself to save sixpence for anything he wants." In another, written a few weeks after his death, Sir Godfrey

says, "I wonder old Dr. Hooke did not choose rather to leave his 12,000*l.* to continue what he had promoted and studied all the days of his life, I mean mathematical experiments, than to have it go to those whom he never saw nor cared for. It is rare that virtuosos die rich, and it is a pity they should, if they were like him." Dr. DUCARREL'S MSS. quoted in *Biog. Dict.* Hooke sometimes declared that he intended to dispose of his estate for the advancement of natural knowledge, and to promote the ends for which the Royal Society was instituted; to build a handsome edifice for the Society's use, with a library, laboratory, and repository, and to endow a professorship. *Life by WALLER.*

§ BRAY'S *Memoirs of Evelyn*, 2nd edit. 4to., vol. ii., p. 268.

BOYLE died in December, 1691, and his funeral sermon was preached by the celebrated Dr. BURNET, at St. Martin's Church, "in which," says EVELYN, "he spake of his wonderful civility to strangers, the great good which he did by his experience in medicine and chemistry, the works, both pious and useful, which he published, the exact life he led, and the happy end he made*."

Upon the whole it may truly be said of BOYLE, that, though he enlightened and adorned the avenues of science, he scarcely enriched it; he wrote much, and generally to the purpose, but he is rather the historian than the actor. It may be remarked however, that in BOYLE, and especially in his contemporary, HOOKE, we have the first genuine samples of the influence of Lord BACON's doctrines, which actuated all their proceedings, and produced effects marvellously beneficial. Mr. BOYLE's Essays on the successfulness and unsuccessfulness of experiments, and the preface to his philosophical writings, are in the genuine spirit of experimental research; and HOOKE, in the preface to the *Micrographia*, has spoken so much to the point, and in language so novel and bold in the then state of science, that, upon perusing it, we are struck with the entire confidence which it bespeaks for his subsequent experimental details.

After adverting to the deep-rooted errors that have been grafted upon science, by the slipperiness of the memory, the rashness of the understanding, and the narrowness of the senses, and showing that these failings may, in some degree, be obviated by the right ordering and rendering them duly subservient to each other, he proceeds to point out the means of tracing the footsteps of nature, "not," as he says, "in her ordinary course only, but also in her doublings and turnings; and in this investigation, upon which the desirable reform in philosophy is to be founded, there is not so much required any strength of imagination, or exactness of method, or depth of contemplation, as a sincere hand and faithful eye, to examine and to record the things themselves as they really appear."

HOOKE then goes on to lament that "the science of nature has been too long made the work of the brain and of the fancy; let it now revert," says he, "to plain and sound observation; and let all intelligence be severely examined; let there be rigour in admitting, strictness in comparing, slowness in debating, and shyness in determining. The understanding is to order all the inferior services of the lower faculties; but yet it is to do this as a lawful master, and not as a tyrant. It must not encroach upon their offices, nor take upon itself the employments which belong to either of them. It must watch the irregularity of the senses, but not go before them, or prevent their information; it must examine, range, and dispose of the bank which is laid up in the memory; but it must be sure to make distinction between the sober and well-collected heap, and the extravagant ideas and mistaken images which there it may sometimes light upon." This is, indeed, the language of Lord BACON, by one who acted as he wrote, for HOOKE was a most diligent experimenter, and has recorded his results with all that cautious sobriety which he advises. "If ever," he says, "I have ventured at small conjectures respecting the causes of the things I have observed, I beseech the reader to

* BRAY's *Memoirs of Evelyn*, *Diary*, vol. ii., p 39.

look upon them only as doubtful problems and uncertain guesses, not as unquestionable conclusions, or matters of unconfutable science."

Among the new views and discoveries of HOOKE, connected with chemistry, and many of which are scattered through the writings of BOYLE, there are none of more importance than those relating to the phenomena of combustion, and to the part which the air performs in that process; and as we are now approaching an epoch of our history at which the appearances presented by burning bodies, and the changes which they undergo, were attentively examined and assiduously inquired into, and in which they were considered as one of the main objects of chemical research, it is right that we distinctly understand HOOKE's notions upon this subject, which will be found wonderfully acute, and remarkable for their boldness, as differing from theories then received; and for correctness as superseding the objections to which the other views are liable.

From the obscure hints in the writings of the alchymists, and from the more decided language of BASIL VALENTINE, PARACELSUS, and other writers of that cast, it appears that the phenomena of combustion were generally referred to the existence of some subtle and highly volatile principle, which, expanded and agitated by heat, produced flame and fire. When metals were exposed to the action of heat, the greater number were observed to alter their appearance, and, losing metallic brilliancy, became converted into an earth-like residue, to which the name of *Calx* was given. It was generally admitted that, in this process, the particles of the combustible were thrown into violent vibrations, and so transformed into heat and light; and such a supposition was natural enough, for it appears to a superficial observer, unacquainted with the results of modern discovery, that the matter burned is in a great number of cases entirely consumed, and that the principal products are light and heat.

A tract, extremely remarkable for the period at which it was written, appeared on this subject in France about, or previous to, the year 1630, relating to the increase of weight sustained by tin and lead during their calcination. LE BRUN having melted two pounds six ounces of tin, found that in six hours the whole had passed into the state of calx, weighing three pounds one ounce; and, being puzzled at the circumstance, he consulted REY, a physician of Perigord, as to its cause, who immediately set about an investigation of the matter, which terminated in explicitly referring the cause of the increase to the fixation of air*.

HOOKE in his investigations, and BOYLE by his experiments with the air-pump, which was now just perfected and coming into use, succeeded not merely in demonstrating the important part performed by the presence of atmospheric air in combustion, but HOOKE carried his inquiries still further, and, in his mind's eye at least, seems to have seen and anticipated the results that were gained at a much later period of chemical science, and established upon less questionable authority.

BOYLE found that a candle, charcoal, sulphur, and some other combustibles, would not burn in the exhausted receiver of his air-pump, which however produced a very imperfect vacuum. When he had pro-

* *Essays de JEAN REY, Docteur en Médecine, sur la Recherche de la Cause pour laquelle l'Estain et le Plomb, augmentent de poids quand on les calcine. Paris, 1717.*

cured a good vacuum, he found that gunpowder would not inflame in it by collision of flint and steel, which he properly attributed to the want of due heat in the sparks resulting from collision; for, on heating the powder in the focus of a lens, it exploded: hence he thought the nitre contained in the gunpowder was concerned in furnishing materials to supply the place of the air*.

HOOKE, in the sixteenth section of the *Micrographia*, relating to charcoal and burned vegetables, observes, that in the ordinary process for making charcoal, the consumption of the wood is prevented by the exclusion of air. The charcoal glows, it is true, but does not burn;—hence, he says, may we learn, that the air is the universal dissolvent of inflammable bodies,—that this dissolution generates heat, which we call fire, as is the case in many other dissolutions,—that this dissolution is made by a substance mixed with the air that is like unto, or the *very same*, as that which is fixed in saltpetre,—that, of the burning body, one portion is turned into air, and another portion is indissoluble,—that the dissolving parts of the air are but few, and hence the atmosphere is like those spirits that have much phlegm mixed with them, and become soon glutted; whereas saltpetre abounds more in those solvent particles, and hence a little will dissolve a great sulphureous body quickly and violently; and as other solvents, though but weak, quickly consume the dissoluble body, if the supply be renovated, so air, applied to a shining body by a bellows, will dissolve it as rapidly as saltpetre. From all which he concludes, that there is no such thing as an *element of fire*, but that flame results from the mutual agency of the volatile parts of combustibles, and a part of the atmosphere.

These although not the very words of HOOKE, but an abridgment of them, contain their unadulterated sense: his expressions show that he had experimented more largely upon the subject, but he was unwilling to extend his account of it till he had completely investigated other parts of the inquiry; he particularly alludes to the use of the air in respiration. I do not, however, find in any of HOOKE's later productions, that he followed up the interesting facts detailed in the *Micrographia*, though in his *Lampas*, published in 1677, he has given a beautiful explanation of the way in which a candle burns: he attributes the light and heat to the action of the air upon the combustible matter of the flame, and shows that the interior of the flame is not luminous, by the simple expedient of viewing its section through a thin piece of glass, or of mica.

The doctrines of HOOKE, concerning the influence of the air in combustion, were further illustrated by JOHN MAYOW†, who, in 1674, published his *Tracts on various Philosophical Subjects*. The date of this work is posterior to that of the *Micrographia*, but anterior to the *Lampas*, and it contains arguments very similar to those promulgated in the former work, without, as far as I have been able to find, any reference to them, or even mention of HOOKE's name. But MAYOW's chemical fame need not be built upon his doctrine of combustion, for he has displayed uncommon talents in various other branches of inquiry.

* New experiments touching the relation betwixt flame and air. BOYLE'S *Works*, 4to., London, 1772, p. 563.

† Born in Cornwall, 1645; died in London, 1679.

While these views were promulgating in England, and chemists were busy in endeavouring to raise a theory of combustion, independent of hypotheses, and founded upon experimental inferences only, BECCHER* and STAHL†, in Germany, were at work upon the same subject, and succeeded in establishing an explanation of combustion, which afterwards made much noise abroad, under the name of the *Phlogistic Theory*; and when we revert to the researches whence this theory, as it was called, arose, they carry with them so plausible and accurate an air, and appear so much less at variance with received doctrines, and known facts, that it is not surprising they should have been adopted in preference to the more abstruse and, as they then appeared, hypothetical explanations of HOOKE and MAYOW.

BECCHER'S *Physica Subterranea*‡ was published at Franckfort in 1669: I have endeavoured in vain to come at the meaning of much of this publication; but thus far is evident, that he has anticipated the prevailing geological theories of the present day, and has argued upon many terrestrial phenomena, with a degree of plausibility and precision which will bear comparison with the more enlightened and learned views of HUTTON and PLAYFAIR.

His notion of the chemical constitution of bodies amounts to this: the elements of bodies are air, water, and three earths, one of which is inflammable, another mercurial, and another fusible. The three earths, combined with water, constitute an universal acid, which is the basis of all other acids. The combination of two earths produces lapideous bodies; and, in the metals, the three earths are united in various proportions. I cannot pretend to explain or elucidate this doctrine, and have no further remark to make upon it, than to request it may be compared with the luminous experiments of HOOKE, in order to set the merits of the latter in their true light.

Towards the end of the seventeenth century, the opinions promulgated by STAHL attained universal assent, and of the names of HOOKE and MAYOW nothing was heard for more than half a century.

* Born at Spire in 1625; died in England, 1685.

† Born in Franconia, 1660; died at Berlin, 1734.

‡ Beccher wrote voluminously upon a great variety of subjects. His principal chemical works are as follows:

1. *Edipus Chemicus*. 2. *Metallurgia, de generatione, refinatione, et perfectione Metallorum*. 3. *Physica Subterranea*, and its various appendices. 4. *Parnassus Medicinalis Illustratus*. 5. *Laboratorium Portatile*. 6. *Chymischer Rosen-garten*.

Beccher's *Edipus* is dedicated to Francis Sylvius Deleboë, who, in 1658, was elected the first Professor of Medicine in the University of Leyden. He was a man of an acute mind, as appears from his various essays and tracts, more especially from his *Prælex Med. Idea Nova*. He died at Leyden in 1672.

"Utilissimum profecto munus subiisti, quo tui auditores non verba, sed corpora, non chymerasticos terminos, verum ipsas reales enchyrises, non inanes denique et immateriales facultates, sed a te demonstrati, effectus causas practicas audiunt, vident, tangunt." Beccher everywhere compliments him as a man not of words, but of deeds; as a philosopher, who eminently sought to render science popular and intelligible to all capacities.

The language of Beccher's *Physica Subterranea* is sufficiently inelegant and incorrect. "Excuso Latinitatem in hoc opere," says he, "quam barbaram esse fateor, ob materiem et ob scriptionem, in specie scriptionis modum: ex ore enim dictantis totum opus conceptum est. Sic rebus attentus, verba neglexi." This is at once an example and apology.

Rejecting the mercurial earth of BECCHER, STAHL retained as elements, water, acid, earth, and fire, or, as he termed it, *Phlogiston*, a principle of extreme tenuity, and prone to a kind of vibratory motion in which it appears as *fire*. He went beyond BECCHER in adducing experimental proofs of his hypothesis. When phosphorus is burned, it produces an acid matter with the evolution of much heat and light; consequently, phosphorus consists of acid and phlogiston: if this acid be now heated with charcoal or other body abounding in phlogiston, phosphorus will be re-produced.

When zinc is heated to redness, it burns with a brilliant flame, and is converted into a white earthy substance or calx. Hence zinc consists of this earth and phlogiston.

Now, it will be observed, that nothing is said here of the increase of weight which REY attributed to the condensation of air, and which MAYOW has as distinctly referred to the fixation of HOOKE'S nitro-aërial particles. Nor is that obstacle taken into the account which BOYLE'S experiments had suggested, and which HOOKE is particularly fond of dwelling upon, namely, that bodies will not burn without air.

However, this hypothesis of STAHL, notwithstanding the increase of weight in the burning body, the requisite presence of air, and other bars against it, was immediately embraced by the generality of chemists, and maintained an unimpeached dominion for upwards of fifty years, until shaken and upset by the arguments of LAVOISIER, who, availing himself of the discoveries of SCHEELE, PRIESTLEY, and BLACK, brought an insuperable mass of evidence to bear against the doctrine of phlogiston*.

That constituent of the air which HOOKE had detected in nitre, and which MAYOW called its nitro-aërial particles, was, under the new title of *oxygen*, regarded as accessory to all cases of combustion. It was presumed that this aërial matter consisted of heat and light, combined with a ponderable base, which united with the combustible, conferring upon it new characters, while the other elements were extricated under the form of fire. But to this explanation two difficulties soon presented themselves; the one, that in many cases of combustion, aëriiform matter, instead of being absorbed and decomposed, is evolved and composed; and the other, that the evolution of heat and light is not proportional to the volume of air condensed, but depends upon the rapidity of the condensation, and upon the nature of the combustible. These objections, however, cannot be fully discussed without a reference to the doctrines of heat, light, and electricity, which must not now be entered upon.

* Stahl's doctrines are very ably set forth in his *Three Hundred Experiments*, published at Berlin in 1731; and in his *Fundamenta Chemicæ*, Nuremberg, 1723 and 1732. He noticed the necessity of air to combustion, but he considered flame or fire as resulting from its violent ethereal agitations. Stahl is continually urging circumspection in hypotheses, yet preconceived opinions are always leading him to erroneous

conclusions, as the following passages amply prove. "Aer ignis est anima, hinc, sine aere nihil potest accendi vel inflammari."—"Aer in motum excitatus, seu ventus artificialis, vel etiam naturalis, mirum excitat motum ætheris seu flammam; hinc ad ignem fusorium, et vitrificatorium, promovendum, foliibus opus est; imo gradus et vehementia ignis dependet multum ex aeris admissione."—*Fund. Chem. dogmat. et ration.*, p. 22.

§ VI.

MAYOW, whose name was mentioned in the last section coupled with that of HOOKE, in researches concerning the influence of air upon combustion, is the first writer who divulged views worth recording upon the subject of respiration, and who has elsewhere displayed some shrewd guesses concerning the causes and effects of chemical affinity. In the first case, he opened a communication between chemistry and physiology; and, in the latter, he extricated a most important and fundamental branch of chemical philosophy from the mire of false reasoning, and planted it in the precincts of experimental research.

MAYOW was the ornament of his time and country as an experimental inquirer; but, unfortunately, he seems to have fallen upon unpropitious ground, and his talents, instead of having been awakened by emulation, were damped by the coldest reception. He was a native of Cornwall, and died at the early age of thirty-five, at the house of an apothecary in York-street, Covent garden. Dr. BEDDOES, and more lately, Dr. YEATS*, have each asserted his claims to several of the discoveries attributed to modern experimenters, and they have in many points made out an irresistible case in his favour.

At an early period of his experiments, MAYOW seems to have been struck with the analogy between the phenomena of combustion, and those of respiration, and although many of his conclusions are full of error, there are more which are correct and even refined. He burned a candle under a bell-glass, and found the air so deteriorated as to be unfit for the continuance of combustion. He then confined a mouse in a similar portion of air, and it soon manifested the want of its renewal. Then, by putting a mouse and a candle under the same bell-glass, he found it live only half the time that it had survived when under the glass alone. He then reversed the experiment, and endeavoured to fire combustible matter in air that had been spoiled by breathing; and finding that it would not burn, he observes, that "the nitro-aërial particles are absorbed both by the candle and the animal†."

Examining the residuary air standing over water after combustion, he found that it was a little lighter than the atmosphere, and extinguished flame; thus remarkably describing nitrogen by its principal properties, namely, that it does not support combustion, that it is not absorbed by water, and that its specific gravity is inferior to that of atmospheric air.

When MAYOW speaks of the *destruction of the elasticity* of a portion of the air, he alludes to its absorption by water; and finding the carbonic acid, formed by respiration and combustion, to be thus absorbed, and its formation always connected with the loss of power to support flame, or of its nitro-aërial parts, he talks of restoration of elasticity by restoring the nitro-aërial matter.

MAYOW also obtained hydrogen gas by acting upon iron by dilute

* *Observations on the Claims of the Moderns to some Discoveries in Chemistry, &c.* By J. D. YEATS, M.D. London, 1798,

† See the 1st and 2d Tracts, *De Sal-nitro, et Spirito Nitro-aërio*, and *De Respiratione*.

sulphuric acid; and nitrous gas, by immersing the same metal in dilute *aquafortis*. Upon the whole, MAYOW's experiments upon respiration, and upon the gases, are something more than ingenious. Considering the novelty of the subject, and the imperfection of his apparatus, they may be considered as surprising efforts of experimental diligence, and his conclusions may be ranked as remarkable indications of a fruitful mind, not wandering amongst hypotheses, but settling upon the results of experiment. Not satisfied with having ascertained that one part only of the atmosphere supports life, he extended his inquiry to the subsequent influence of that part upon the system. It was the prevailing notion of his time that respiration cooled the blood, but having observed in the nitro-aërial or fire-air particles an essential to flame and fire, he considered their absorption as necessarily connected with the heat of the blood; he observed an analogy between the respiration of animals and that of plants; and to show the existence of air in the blood, he had recourse to the air-pump, which, he says, extricates it more copiously from arterial than from venous blood.

The most remarkable Chapter, however, of MAYOW's tract, is that relating to the "mutual action of salts of contrary kinds," or, in other words, to chemical combination and decomposition, a subject which he has handled in so masterly a manner, and which is so ably supported by experiments, that, although anticipated in respect to his researches on the air by HOOKE, we must here give him due credit as an original inquirer.

It was imagined by those predecessors of MAYOW who expounded their notions respecting chemical affinity, that bodies combined in consequence of certain mechanical forms of their particles; and that when an acid was added to an alkali, the salt produced was a perfectly new product, resulting from the *annihilation* of the particles of its components. It was not admitted, or at least not generally admitted, that the acid and alkali existed as such, and might again be separated from the neutral salt. MAYOW first set about rectifying this gross error. When spirit of salt, he says, is mixed with *sal volatile*, sal ammoniac is produced, in which, it is true, neither the properties of acid, nor of alkali, are apparent; yet, if salt of tartar be distilled with sal ammoniac, the volatile alkali will be displaced with all its previous characters, because there is a greater attraction between spirit of salt and tartar than between spirit of salt and volatile alkali. Again, to show that the acid is not destroyed in saline combinations, he instances the decomposition of nitre by oil of vitriol, which, he says, displaces the nitric acid, and the residuum in the retort furnishes vitriolated tartar. It may be asked, he says, why, when nitre is heated, the nitric acid does not rise, for it is, as we have just seen, very volatile: the reason is, that it is restrained and kept down by its attraction for the tartar, and can only be displaced by bodies which have a stronger attraction for tartar than it. This is excellent reasoning, and it would be difficult, with all the advantages of modern acquisitions, to adduce two more illustrative cases than those which MAYOW has furnished. He then goes on to show that acids have a greater attraction for alkalies than for metals. The metals, he says, are soluble in one or other of the acids, but their solutions are decomposed by salt of tartar; the acid then combines with the tartar, and the metal is precipitated. In the same way

alkali unites to sulphur; but if this combination be dissolved in water, and acid added to the solution, the sulphur falls, and the acid and alkali unite. Combinations of the metals with sulphur are also decomposed by acids; thus, if sulphuret of antimony be distilled with aquafortis, the acid and metal combine, and sulphur sublimes.

Having given other similar instances of the combination of sulphur with metals and alkalies, he proceeds to some general views connected with the subject, among which the following deserve particular notice. Although, he says, sulphur enters into these combinations, we are not to imagine, as some have done, that sulphur includes an acid, and thence derives its powers of combination, in consequence of its containing an opposite nature; on the other hand, it is clear, he adds, that the combination is independent of any such hidden cause, and is the mere result of the mutual affinity of the substances. He then cautions those concerned in the compounding of medicines, to beware of the new compounds that may result in consequence of these mutual attractions and decompositions, for "one substance may destroy the efficacy of another, and something perfectly different from the original may result." It is curious, he remarks, that when acid of vitriol is poured upon salt of tartar, so as to form vitriolated tartar, a great effervescence ensues; but if the acid be previously combined with a metal, this is not observed, and yet vitriolated tartar is equally formed; as when salt of tartar is added to solution of green vitriol. In these cases, he says, the acid part of the salt of tartar is retained by the metal; thus giving an explicit account of a frequently occurring case of double decomposition.

These views, relating to chemical attraction, are at once clever and correct, and their merit will be especially enhanced by a comparison with the absurd and groundless speculations previously entertained upon this subject. But MAYOW has other and more weighty evidence in his favour, for it is remarkable that his views and language were adopted by NEWTON, and that the sketch of a theory of chemical attraction given by that philosopher in the Queries annexed to the third book of Optics, is nearly in the language, and quite in the spirit and meaning, of his predecessor MAYOW. The following are a few of the points urged by NEWTON in the explication of these phenomena:—

If carbonate of potash be exposed to air it deliquesces, in consequence, says NEWTON, of an attraction between the salt and the particles of water contained in the atmosphere. And why does not common salt and saltpetre deliquesce in the same way, except for want of such attraction?

And again, where he especially comes in contact with MAYOW, he says, when spirit of vitriol, poured upon common salt or saltpetre, makes an ebullition, and affords on distillation the muriatic and nitric acids, the acid part of the spirit of vitriol staying behind, does not this argue that the fixed alkali in the common salt and saltpetre attracts the acid spirit of the vitriol more strongly than its own spirit, and not being able to hold them both, lets go its own? How these attractions may be performed, continues NEWTON, I do not here consider; what I call *attraction* may be performed by impulse, or by some other means unknown to me: I use that word to signify any force by which bodies tend towards one another, whatever be the cause. Thus, he says, muriatic acid unites to

salt of tartar, by virtue of their respective attractions; but when oil of vitriol is poured upon this compound, the former acid is displaced by the superior attraction of the latter. Silver is separated from aquafortis by quicksilver; quicksilver by copper; and copper by iron; which argues that the acid particles of the aquafortis are attracted more strongly by iron than by copper; by copper than by quicksilver; and by quicksilver than by silver*. Thus, then, chiefly by the experimental labours of MAYOW, and the sagacious views of NEWTON, the old and prevailing notions of the atomic forms of bodies, the hypothesis of hooks, rings, points, and wedges, by which the component parts of bodies were supposed to be held united, gave way to a simple and independent expression of facts.

It has often been said, that anticipations of modern discoveries which could alone be demonstrated by the progress of experimental research, are characteristic of the writings of NEWTON, and proofs of his sagacity and penetration: he inferred that the diamond consisted of inflammable matter, and suspected the existence of a combustible element in water, very long before either of those subjects had been experimentally investigated; and in his notions relating to the subject of chemical attraction, he has an anticipation not less striking, relating to the connexion between chemical and electrical attraction. "The attractions of gravity, magnetism, and electricity, reach to very sensible distances, and so have been observed by vulgar eyes; and there may be others which reach to so small distances as hitherto to escape observation, and perhaps electrical attraction may reach to such small distances without being excited by friction†."

I shall conclude this subject with some account of the progress more lately made in elucidating the doctrines of chemical attraction.

In 1718, GEOFFROY‡ invented those tables of affinity which are now often given in elementary works, and which have proved of service in extending chemical knowledge; he considered the order in which bodies separate each other from a given body, as constant. Thus, he thought the metals were always separated from acids by the absorbent earths, these by volatile alkali, and the volatile by the fixed alkalies; to represent, therefore, the attraction of acids for these substances, he placed them at the head of a column, with the other bodies beneath, in the order of attraction, as shown in the margin.

He then constructed a column for each particular acid; thus the table for nitric acid taken from NEWTON's experiments would stand as annexed:—

GELLERT and LIMBOURG, in 1751 and 1758, extended and, in some respects, improved these tabular representations of the results of attraction; but no considerable progress was made in the investigations connected with the subject, until BERGMAN published his dissertation upon it in 1775.

ACIDS.

Fixed alkalies.
Volatile alkali.
Absorbent earths.
Metals.

NITRIC ACID.

Fixed alkali.
Volatile alkali.
Earths.
Iron.
Copper.
Lead.
Mercury.
Silver.

* NEWTON'S *Optics*, book iii., query | 31.

† *Optics*, book iii.
‡ *Mem.*, Paris, 1718.

Of BERGMAN'S character and merits as a chemist, I shall speak afterwards, confining myself at present to the views which he entertained upon the subject of affinity, or, as he called it, *elective attraction**.

BERGMAN considered that every substance possessed a peculiar attractive force for every other substance with which it combines; a force capable of being represented numerically: he regarded decomposition as complete; that is, whenever a third body *c* is added to a compound *a, b*, for one of the constituents of which it has a stronger attraction than that which already exists between them, the compound will be decomposed, and the whole of one of its elements transferred to the added body. Thus, suppose the attraction of *a* for *b* to be represented by 1, and of *a* for *c* by 2, then the addition of *c* to *a b* will produce the compound *a c*, and *b* will be separated. When lime-water is added to nitrate of magnesia, the latter earth is precipitated, and the former combines with the nitric acid. Hence, nitric acid poured upon a mixture of lime and magnesia, dissolves the former, in preference to the latter earth.

The observation of these facts led BERGMAN to call this kind of attraction *elective*, and he has given tables, showing these relative attractions of bodies in the dry and humid way. Thus:

BERGMAN'S opinions relating to affinity were generally admitted as correct, till BERTHOLLET published his work on *Chemical Statics* in 1803, in which he endeavoured

SILVER.	OXIDE OF SILVER.
Lead.	Sulphuric acid.
Copper.	Oxalic do.
Mercury.	Phosphoric do.
Bismuth.	Nitric do.
Tin.	Tartaric do.
Gold.	Citric do.

to revive, under a new aspect, some of the old chemico-mechanical doctrines, and to prove that the forms of the acting particles, and their magnitude, or masses of matter, were concerned in influencing the results. Though these doctrines may now be considered as disproved, they had many advocates, and were gaining ground, until the promulgation of the theory of definite proportionals. The experiments adduced by BERTHOLLET in support of his hypothesis, appeared at first very satisfactory; but upon minute inspection they have their weak points, and many of the errors into which they led have been successfully unravelled by Professor PFAFF, of Kiel; by Sir H. DAVY, and others. In illustration of the agency of the mass of matter, BERTHOLLET has adduced the mutual action of sulphate of potassa and baryta: when solution of baryta is added to sulphate of potassa, potassa is liberated; and sulphate of baryta is formed and precipitated insoluble; but if a large quantity of potassa be added to a small quantity of sulphate of baryta, the mass will, according to BERTHOLLET, prevail over what appears to be the real chemical affinity, and sulphate of potassa will be formed, and baryta evolved. But Sir H. DAVY pointed out the fallacy to which this experiment is liable, by showing that pure potassa does not effect any change upon sulphate of baryta, but that, making the experiment in open vessels, part of the potassa acquires carbonic acid, and then a double affinity is brought into action, the bodies present being carbonate of potassa and sulphate of baryta†.

* *De Attractionibus Electivis. Opus-*
cula, vol. iii., p. 291.

† *Elements of Chem. Philos.*, p. 119.

BERTHOLLET's notion, that the acting bodies are divided among each other in proportions, depending upon their relative masses and attractions, has been combated and disproved by PFAFF*, who has shown that tartrate of lime is completely decomposed, by adding to it a quantity of sulphuric acid, exactly sufficient to saturate the lime it contains; and in the same way he has shown that oxalate of lead is decomposed, by adding sulphuric acid sufficient to saturate the oxide of lead.

But the establishment of the Atomic Theory, from which we learn that bodies combine only in certain definite proportions, has gone further to elucidate the important subject of chemical attraction, and to subvert former doctrines, than any previous objections or partial experimental investigations. In establishing this theory, all the eminent chemists of Europe have taken an active part. Its foundation was apparently laid by Mr. William Higgins of Dublin, previous to the year 1789; for the essential facts, which have subsequently been followed up, and worked out by later chemists, are to be found in his *Comparative View of the Phlogistic and Antiphlogistic Theories*. In the year 1814, he published his *Experiments and Observations on the Atomic Theory*, to which I may also refer the historical reader.

Between the years 1792 and 1802, Dr. RICHTER†, of Berlin, published his *Geometry of the Chemical Elements*, containing a series of tables, showing the weight of each base capable of saturating one hundred parts of each acid; and the weight of each acid capable of saturating one hundred of each base. He observed, that in all these tables the bases and the acids followed the same order: and further, that the numbers in each table constitute a series having the same ratio to each other in all the tables. Thus, supposing in the table of sulphates, one hundred parts of acid were saturated by one hundred of soda, two hundred of potassa, and three hundred of baryta; then in the table of nitrates the same ratio would hold good, and the soda, potassa, and baryta would there also stand to each other in the relation of one, two, and three.

Thus was explained why, when two neutral salts decomposed each other, the newly formed salts are also neutral; for the same *proportion* of bases that saturate a given weight of one acid, saturate a given weight also of all the other acids. Hence numbers may be attached to each acid and to each base, indicating the weight of it which will saturate the numbers attached to all the other acids and bases. Upon this principle, elementary works on chemistry contain tables of the representative or equivalent numbers of bodies; and upon the same principle, Dr. WOLLASTON, by adapting such table of numbers to a moveable scale, on the principle of GUNTER's sliding rule, has constructed the *logometric scale of chemical equivalents*, which is so important and valuable an instrument to the practical chemist.

I cannot enter into further details respecting the researches which have established and elucidated this highly important subject, without entering into discussions involving the labours of contemporary chemists; and must, therefore, here, merely refer to the investigations of Dalton‡

* *Annales de Chimie*. LXXVII.

† *Anfangsgründe der Stöchiometrie oder*

Messkunst Chemischer Elemente.

‡ *New System of Chemical Philosophy*.

and Gay Lussac* connected with it, and to the details which will be found in another part of this work.

§ VII.

BEFORE we proceed with the regular thread of our historical sketch which is now carrying us into that eventful period for chemistry, and indeed for the progress of all the sciences, the first half of the eighteenth century, it is requisite rapidly to review some collateral investigations which occupied the philosophers of the seventeenth century, and which, though not strictly chemical, contributed much to the progress and perfection of some of the more difficult and abstruse branches of that department of knowledge.

Of these inquiries it will especially be right to notice such as relate to the phenomena and effects of *heat*, which, in consequence chiefly of the invention of the *thermometer*, were pursued with a degree of ardour and success, highly creditable to the diligence and sagacity of the individuals concerned. Among them, BOYLE is entitled to particular praise; and though his inquiries are blended with much irrelevant and miscellaneous digression, they contain materials amply important and interesting; materials which paved the way for some of the most eminent achievements in chemical science.

It has been disputed to whom the honour of inventing the thermometer belongs; some have given it to CORNELIUS DREBBEL†, and some, with more plausibility, to SANTORIO‡ of Padua. But, when we reflect upon the imperfection and comparative uselessness of the instruments attributed to those claimants, and when the construction of the thermometer now in use may be indisputably referred to the Florentine Academicians, the disputes respecting priority become of little importance. Air was first used as a means of exhibiting, by its expansion and contraction, the alternations of heat and cold; and VAN HELMONT has described, with some minuteness, several modifications of the *air thermometer*§. But however valuable such thermometers may be for particular purposes, they are rendered extremely inconvenient by the rapid and great dilatibility of air by moderate changes of temperature: besides which, it is very difficult so to construct air thermometers as to agree among themselves in indicating the same degree, when applied to bodies of similar temperature. The Academicians del Cimento were the first to employ thermometers constructed as we now see them. They used tubes, with a bulb containing spirit of wine, and closed so as to exclude the influence of air, and prevent the evaporation of the liquid. This thermometer, however, though much superior to, and more useful than the old air thermometer, was yet an useless instrument, if we speak of it comparatively with those now constructed; for, there being no fixed point at either extremity of the scale, the graduation was arbitrary, and no two instruments, when placed in an atmosphere of the same temperature, indicated the same degree of heat.

* *Mémoires d'Arcueil*, ii. 287.

† Born in Holland, 1572; died in London, 1634. He is also said to have invented the microscope.

‡ Born at Capo d'Istria, 1561; died at Venice, 1636.

§ *Opera Omnia*, Art. Aër, p. 61.

There is some confusion in this part of the history of the thermometer, for, though the Florentine Academicians state that their scale generally commenced at the temperature of freezing, they represent that point by various terms or degrees, unsusceptible of comparison, and say nothing of the differing temperature of ice, which may exist at 32° , or any inferior degree. In Italy, however, it is most probable that the ice was in a thawing state, and therefore about 32° of FAHRENHEIT'S scale; but all registers of the weather, and all enumerations of high and low temperatures, are quite unintelligible, as recorded by the experimentalists of that period.

"The great and truly honourable Mr. BOYLE" turned his mind with much earnestness to the construction of a *scale* for thermometers, and seems to have had it in contemplation to set out with the temperature at which water *begins* to freeze; "but the objections which he apprehended might be made to this method scared him so much," says Dr. MARTINE*, "that he prosecuted no further this consideration of fixing a standard for making and graduating thermometers all in the same way." Dr. HALLEY† observed, that the same thermometer always indicated the same temperature in places deep under ground, where neither the heat of summer nor the cold of winter seemed to produce any effect; and MARRIOTTE and DE LA HIRE had made the same remark upon thermometers placed in the caves of the observatory at Paris. But Dr. MARTINE, whose authority is, in most respects, very exact, gives Dr. HALLEY the merit of fixing upon the boiling point of water as a standard of graduation, which elevates the quicksilver in the thermometer tube always to a given point, under given barometrical pressure; and the mean pressure of 30 inches of mercury is generally understood to be that to which our thermometers are graduated. Sir I. NEWTON employed the freezing and boiling of water as fixed points, but he used linseed oil to fill his tubes, a liquid inconvenient from its viscosity, and irregularity of expansion. Alcohol was first used by the Florentine Academicians, because it is very sensible to changes of temperature, and remains clear in the tube; but, since its boiling point is much below that of water, it is useless for the measurement of high temperatures, though, from not freezing, well suited to indicate extreme cold. For general convenience and equability of expansion, mercury, first used, I believe, by Dr. HALLEY, takes precedence of all other liquids. It bears nearly a red heat before it boils, and sustains the cold of these latitudes without freezing; hence it is the liquid generally used for accurate and delicate thermometers.

The principal thermometric scales in use in Europe are, FAHRENHEIT'S, which commences at the temperature produced by mixing snow and salt, and which is 32° below the freezing of water, so that the latter point is marked 32° , and the boiling point 212° , the intermediate space being divided into 180° : REAUMUR'S, in which the zero is the freezing point, and 80° the boiling point: and the *Centigrade*, in which the space between the freezing and boiling of water is divided into 100° , the freezing point being 0° and the boiling point of water 100° .

In this country, FAHRENHEIT'S scale is in general use; over the greater part of Germany, REAUMUR'S scale is employed; and in France, the *Centi-*

* *Essays, Medical and Philosophical.* | † *Phil. Trans.*, Abr. ii., p. 36.
By G. MARTINE, M.D, London, 1740.

grade: it is much to be desired that the subject of a thermometric scale should, in the present advanced state of science as regards the doctrine of heat, be taken into consideration, and that either the *Centigrade* (which is certainly the least objectionable of those hitherto used) or some analogous scale should be universally employed.

There are other circumstances connected with the construction and indications of the thermometer, which I reserve for notice till we consider the more refined investigations relating to the subject of heat, undertaken at a subsequent period: in the meantime we may advert to the discovery of a singular property possessed by water, which, as far as concerns the influence of heat upon it, distinguishes it from other liquids. This anomaly was first observed by the Florentine Academicians: "We know," they say, "that water, in passing into the state of ice, suffers great expansion, a fact sufficiently evident from the violence with which various vessels are broken and rent asunder during the freezing of water in them; but it was not known to us at what particular period of refrigeration this expansion occurs; nor could we learn it from our former experiments, which were made in vessels of silver, gold, brass, and other strong, but opaque materials. We, therefore, now employed glass flasks, and observed, that the moment they were immersed in ice, the water in the neck of the flask was suddenly elevated, that it then began gradually to fall, and at length remained for a few moments quite stationary; then it began again to rise with a slow, but apparently equable progress at first, but afterwards sprung up so suddenly, that the eye could scarcely follow it*."

In BIRCH's *History of the Royal Society*, under the date of the 6th of February, 1683, we find some experiments on the freezing of water made

* The following unaffected narrative of this celebrated experiment is very different from the usual verbose and pompous style of the philosophers of the period.

"Già sapevamo per innanzi (e lo sa ognuno) che il freddo da principio opera in tutti i liquori ristignimento, e diminuzione di mole, e di ciò non solamente n'avevamo la riprova ordinaria dell' aquarzente de' Termometri, ma n'avevamo fatta esperienza nell' acqua, nell' olio, nell' argentovivo, ed in molti altri fluidi. Dall' altro canto sapevamo ancora, che nel passaggio, che fa l' acqua dall' esser semplicemente fredda al rimuoversi dalla sua fluidità, e ricever consistenza, e durezza coll' agghiacciamento, non solo ritorna alla mole, ch' ell' aveva prima di raffreddarsi, ma trapassa ad una maggiore, mentre se le veggono rompere vasi di vetro e di metallo con tanta forza. Ma qual poi si fosse il periodo di queste varie alterazioni, che in essa opera il freddo, questo non sapevamo ancora, ne era possibile d'arrivarvi con agghiacciarla dentro a' vasi opachi, come quei d'ar-

gento, d'ottone, e d'oro, ne quali s'era fin' allora agghiacciata: Onde per non mancare di quella notizia, che pareva esser l'anima di tutte quest' esperienze, ricorremmo al cristallo, ed al vetro, sperando per la trasparenza della materia d'aver presto add' assicurarci come la cosa andasse, mentre si poteva a ciascun movimento, che fosse apparso nell' acqua del collo, cavar subito la palla dal ghiaccio, e riconoscer in essa quali alterazioni gli corrispondessero. Ma la verità si è, che noi stentammo assai più che non ci saremmo mai dati ad intendere, prima di poter rinvenire alcuna cosa di certo intorno a' periodi di questi accidenti. E per dirne più distintamente, il successo è da sapere, che nella prima immersione, che facevamo della palla, subito, ch' ella toccava l'acqua del ghiaccio s'osservava nell' acqua del collo un piccolo sollevamento, ma assai veloce, dopo il quale con moto assai ordinato, e di mezzana velocità s'andava ritirando verso la palla, finchè arrivata a un certo grado non proseguiva più oltre a discendere, ma si fermava quivi per qualche tempo, a

before that body, in consequence of a letter received from Mr. MUSGRAVE, of Oxford. "Dr. CROUNE said, he had observed water put into a bolt-head rise higher before freezing. Mr. HOOKE attributed this to the shrinking of the glass. Dr. C. said, the glass had been long in the cold before, and the water rose immediately. Dr. WALLIS proposed that an empty glass might be well cooled in a freezing liquor, in order that it might have its contraction before the water be put into it. This was done immediately by Mr. HUNT, and the water being put into a small bolt-head rose in the neck." Numerous and correct experiments have completely established this peculiarity in the freezing of water; other fluids have their maximum of density just before the freezing point; water expands before it freezes, and consequently water at 36° is lighter than water at 40° , and floats upon its surface; hence it is, that large masses of water, being cooled by the atmosphere upon their surface, only freeze there, and the water beneath retains the more congenial temperature of 40° .

Among the experiments made by the *Accademia del Cimento*, we find many details independent of those already adverted to, which are at once accurate and curious, and especially in that section of their *Transactions*, entitled *Experiments relating to Ice*. In the sixth experiment of this section they notice the effect of various metallic vessels upon the thawing of ice: they found it was longer preserved in lead and tin than in similar vessels of brass and of iron; and that it soon thawed in gold, and sooner in silver. This enumeration of the metals is in the order of their conducting power, as ascertained more than a century afterwards by Dr. INGENHOUSZ.

The radiation, reflection, and refraction of heat, are subjects of inquiry which also probably engaged much of the attention of the Florentine experimentalists, but their published essays contain scarcely any details relating to them. In the ninth experiment, however, of the above quoted section, they have given an account of a discovery that afterwards excited much discussion, relating to the reflection and radiation of cold. "We were anxious to try if a concave mirror, placed before a mass of ice, weighing five hundred pounds, caused any reflection of cold upon a very delicate thermometer placed in its focus; and truly it began immediately to fall; but in consequence of the vicinity of the ice, it was doubtful whether the effect resulted from the direct or from the reflected rays; we, therefore, covered the mirror, and whatever was the cause, certain it is that the spirit began immediately to rise again. With all this, we do not mean positively to affirm that no other cause could have produced such an effect than the absence of the rays reflected from the mirror, for we were not careful in adopting all the precautions requisite in such an experiment*."

giudizio degli occhi, affatto priva di movimento. Poi a poco a poco si vedea ricominciare a salire, ma con un moto tardissimo, e apparentemente equabile, dal quale senz'alcun proporzionale acceleramento spiccava in un subito un furiosissimo salto, nel qual tempo era impossibile tenerle dietro coll'occhio, scorrendo con quell'impeto, per così dire,

in istanti le decine e le decine de' gradi. *Esperienze intorno al progresso degli artificiali agghiacciamenti, e de' loro mirabili accidenti. Saggi di naturali esperienze fatte nell'accademia Del Cimento.*—Firenze, 1691.

* *Saggi*, above quoted. See also Waller's Translation of the *Essays of the Academicians del Cimento*. 1684.

MUSCHENBROEK, DE MAIRAN, and others, concluded from these and similar experiments, that cold is not the mere absence of heat, but a distinct form of matter possessed of specific properties. Sometimes it has been spoken of as a substance of a saline nature, floating in minute particles in the air, and occasioning the congelation of water by intruding themselves among its particles. Now, although such a conclusion is not called for by the phenomena, it has been plausibly conjectured that ice and other cold bodies do radiate matter, which is capable of exciting the sensation of cold in circumjacent bodies.

To get rid, however, of such an hypothesis, it has been suggested that the effect of the ice is to disturb the balance of temperature in the surrounding bodies, and consequently to cause a chasm, as it were, into which they tend to pour their excess of heat; among these is the thermometer, which consequently indicates cold: but although such an explanation might suffice in respect to the mere approximation of the ice to the thermometer, it is scarcely applicable to the case of radiation.

Sir H. DAVY says, "the apparent radiation of cold is in harmony with the phenomena of the reflection of the solar beams; for if it be supposed that rays capable of producing heat emanate from all terrestrial bodies, but in quantities greater in some increasing proportion as their temperatures are higher, then the introduction of a cold body into the focus of one mirror ought to diminish the temperature of a thermometer in the focus of the other, in the same manner as a black body placed in one focus would diminish the quantity of light in the other focus; and the eye is to the rays producing light, a measure similar to that which the thermometer is to rays producing heat*."

LESLIE admits that the temperature excited by radiant matter varies with its source, and that all substances may be considered as producing these emanations. If we approach a heated surface, we feel the radiant heat; if the surface be of the same temperature as ordinary circumjacent bodies, or of a temperature between 40° and 80° , we feel, perhaps, nothing remarkable; yet such a surface does actually radiate matter of its own temperature, as shown by approaching it with a cooler thermometer: if the surface be of ice or colder materials, we feel upon approaching it the sensation of cold, depending upon the emanation of cold radiant matter, since it is susceptible of reflection by the mirrors. We are further to consider, that the terms *heat* and *cold* are merely relative. We may suppose that in an atmosphere heated to 400° , boiling water would radiate (comparatively speaking) cold; and in the same way ice at 32° would radiate heat in an atmosphere very much below the freezing point. To LESLIE we are indebted for an admirable series of researches on the philosophy of radiant matter, partly contained in his *Treatise on Heat*, and partly in other essays, (*Suppl. to Encyclop. Brit.*) He supports the theory of the radiation of cold by some striking illustrations.

§ VIII.

FROM the preceding details, some idea may be formed of the state of chemistry at the close of the seventeenth century. As an art, we have

* *Elements of Chemical Philosophy*, p. 206.

seen with what success and diligence it was cultivated by BASIL VALENTINE and GLAUBER; and how ably it was pursued as a science by MAYOW and HOOKE. To these philosophers, and to a few of their companions, we not only owe the materials which were arranged and embodied by their earliest successors in the eighteenth century, but we are to ascribe also to them the merit of founding scientific chemistry; of laying the basis upon which the superstructure of modern chemical science has been raised. The importance of multiplied observations and experiments, the application of chemical principles to agriculture, and the aid to be derived from them in several arts and manufactures, as well as in many departments of domestic economy, are to be learned in the writings of GLAUBER; while BASIL VALENTINE and VAN HELMONT have shown the necessity of studying pharmacy on chemical principles, and have applied, with much success, the doctrines learnt in the laboratory, to the preparation of many invaluable medicines, which have facilitated the treatment and cure of disease; nor were the quackery and eccentricities of PARACELSUS unemployed in this reformation. In that age, example was more efficacious than precept; and those who witnessed the cures which he performed, enlisted under his banner, and were equally vehement with their leader in combating the doctrines of the Galenical school of physic, and substituting those of the chemical sect.

If we look at the scientific generalizations of modern chemistry, and more especially at the theories of combustion and acidification promulgated by the French school, about the middle of the last century, we find them not anticipated merely, but even minutely explained, by BOYLE, HOOKE, and MAYOW, who flourished about one hundred years before LAVOISIER; and MAYOW, in his researches into the laws and phenomena of chemical affinity, seems to have trodden upon ground which even NEWTON explored as his own. In the history of chemistry, we perceive perhaps, more than in any other branch of science, the different roads by which the human mind arrives at the same conclusions; but we are not therefore to consider those conclusions as unavailing, because anticipated; the very circumstance of attaining them by different means, justifies the search; and he whose investigations disclose new views, and unfold new truths, may rest satisfied that he has not laboured in vain, because he ultimately arrives where others have been before him. In estimating, however, the true merits of chemical discoveries and inventions, and more especially in determining the excellence and originality of theories, it is requisite to look to their sources, and to examine the steps which lead to them, and upon that examination to found our opinion.

The leading feature and important novelty of the science, as influencing its progress in the last century, was certainly the discovery of gaseous bodies, and the perfection of pneumatic chemistry; without which analysis could have made little progress, and, independent of which, all improvement in theory would have been but slow and ineffectual; it was also materially, though less directly assisted by those investigations respecting the agency of heat, in which Dr. BLACK made himself so eminent.

Though something is due to MAYOW, we must in justice confer the merit of founding *pneumatic chemistry* upon Dr. STEPHEN HALES*, whose

* Born in Kent, 1677; died at Teddington, 1761.

researches came before the public very early in the last century. "He refused a canonry of Windsor, that he might continue to devote himself to his parochial duties, and favourite scientific pursuits; and, as piety, truth, and virtue, were the principles of his character, he lived in universal esteem to the age of eighty-four, dying at Teddington, on the 4th of January, 1761, where he was buried, under the church-tower, which he had rebuilt at his own expense."

Dr. HALES commenced the communication of his researches to the Royal Society about the year 1717, and, in 1727, he published his *Statistical Essays, containing an Essay towards a Natural History of Vegetation, of use to those who are curious in the Culture and Improvement of Gardening: also a Specimen of an Attempt to analyse the Air, by a great variety of Chemico-Statistical Experiments, which were read at several Meetings before the Royal Society*. In 1733, a second volume of these Essays was published, containing *Hæmastatics, and Experiments on the Stone of the Kidney and Bladder*. Of these Essays, it will be first necessary to advert to the contents of those relating to the analysis of the air, a term, by the way, which by no means well applies to the researches they contain.

Dr. HALES employed several methods of collecting and examining the gaseous products of a variety of bodies, many of which approach those at present in use. Sometimes he placed substances upon a stand, under a bell-glass inverted over water; or he employed a flask to contain the materials producing æriform matter, over which was placed a bell-glass, the whole being confined over water as before. Or where a high temperature was required for the production of the gaseous bodies, he used an iron retort formed of a bent gun-barrel, and received the air into a vessel inverted in a tub of water. In the modification and management of these forms of apparatus, he displayed some ingenuity; but it should be remembered that he was anticipated in the greater number of his contrivances by MAYOW, as we have already had occasion to remark.

In prosecuting his inquiries by these means, Dr. HALES stumbled upon a variety of curious facts and observations; but having unluckily predetermined that the various products formed were mere modifications and contaminations of common air, he let slip a numerous series of discoveries once fairly within his grasp, and which were afterwards eagerly amassed and successfully reasoned upon by PRIESTLEY and his contemporaries. Thus, Dr. HALES observed that phosphorus when burned, absorbed air, and produced white fumes; but he neglected any examination of the product and of the residue. He distilled air from wood, and found it fatal to animals; from Newcastle coal he obtained one-third its weight of gas; from nitre, one hundred and eighty times its bulk; and from salt of tartar urged by an intense heat, he also procured æriform matter; but in no one instance did he examine these gaseous products with the attention that might have been expected from an experimentalist so diligent and original. He found that iron filings and oil of vitriol produced scarcely any air; but that, upon the addition of water, gas was abundantly evolved from such a mixture. Here he obtained hydrogen, but instead of stopping to examine its properties, he hastens on to irrelevant observations, and seems always eager rather to multiply experiments

than to examine their results. Upon the same principle, he accurately details the quantity of air generated by distilling hog's blood, tallow, sal ammoniac, oyster-shells, Indian wheat, pease, mustard-seed, amber, tobacco, sugar, bees' wax, and gall-stones; and yet, from such numerous experiments, he scarcely draws a single inference that deserves to be recorded.

In his experiments on respiration, Dr. HALES obtained results of such interest, that one is surprised at the coldness with which he pursued them, and the carelessness with which he drops the inquiry. Finding that a given portion of air could only be respired for a given time, and that it soon produced oppression and difficulty of breathing, in consequence, as he says, "of the gross and sulphureous vapours with which it becomes loaded," he endeavoured to discover some substance which, by absorbing those vapours, might render respired air more fit for breathing, and consequently contribute to its purification in small and crowded rooms, and other similar situations. The apparatus which he used in these researches was sufficiently ingenious; it consisted of a bag made of bladder, with a mouth-piece so supplied with valves as to oblige the air breathed into it to traverse its whole length, before it could return to the lungs. He found that he could breathe the air contained in this apparatus to and fro, for a minute and a half; he then wetted certain diaphragms or partitions of flannel in the bag, with different liquids, and found that he was thus enabled to respire the confined air for rather a longer time; but having dipped them in a solution of highly calcined tartar, he found he could, without much inconvenience, continue the breathing for eight minutes and a half.

It is probable that the air was purified in this instance by the absorption of the carbonic acid; or to use Dr. HALES' language, "of the sulphureous gross vapours;" but, unwilling as he always appears to follow up and investigate the new facts, he says, that the effect was perhaps owing to the bladder and syphon being entirely dry, or to some unheeded passage for the air through the ligatures,—“neither did I care to ascertain the matter by repeated experiments, fearing I might thereby some way injure my lungs.” He however weighed the diaphragms, and found that they had increased in weight about thirty grains in five minutes, making the quantity of matter absorbed by them from the expired air, amount to nineteen ounces in twenty-four hours. In other experiments, the author notices the purification of air spoiled by the burning of candles and of brimstone, by the action of calcined tartar; but he takes no pains to inquire into the specific action of the salt, and confounds it with that of saline bodies generally.

But Dr. HALES' researches relating to the motion of sap in vegetables, are in a great measure free from the objections which may be made to his other experimental inquiries, and were pursued upon a more regular and digested plan. His first object seems to have been to ascertain the quantities of matter imbibed or perspired by plants and trees; for this purpose he grew a sunflower in soil contained in a tight box, and watering it with given weights of water, he ascertained the quantity that it daily lost by transpiration from the leaves: after stating the extent of surface of the leaves, he informs us, that its minimum of loss by that chan-

nel was sixteen ounces, and its maximum twenty-eight ounces, in a day of twelve hours. To ascertain more particularly the influence of the leaves upon the absorption of water by the root, two branches, one with and one without leaves, were put into separate glasses, containing known quantities of water. The boughs with leaves absorbed on an average from twenty to twenty-five ounces in a day, and were lighter at night than in the morning; those without leaves imbibed but one ounce, and were heavier in the evening than in the morning. This experiment led to the inference, that the ascent of the sap, and the quantity of matter absorbed from the soil, are much influenced by the leaves; "and accordingly I observe," he says, "that the leaves next adjoining to blossoms are in the Spring very much expanded, when the other leaves on barren shoots are but beginning to shoot; and that all peach-leaves are pretty large before the blossom goes off: and that in apples or pears, the leaves are one-third or half-grown before the blossom blows: so provident is Nature in making timely provision for the nourishing of the yet embryo fruit." A certain degree of dryness of air is requisite to promote the due transpiration by the leaves, for when too much moisture hovers about the plant, it hinders the kindly action of the leaves, "whereby," says Dr. HALES, "the stagnating sap corrupts and breeds mouldy fen, which often spoils vast quantities of flourishing hop-grounds. This was the case in the year 1723, when ten or fourteen days' almost continual rain fell, about the latter half of July, after four months' dry weather; upon which the most flourishing and promising hops were all infected with mould or fen in their leaves and fruit, while the then poor and unpromising hops escaped and produced plenty, because they being small did not perspire so great a quantity as the others." "This rain on the then warm earth made the grass shoot out as fast as if it were in a hot-bed, and the apples grew so precipitately, that they were of a very flashy constitution, so as to rot more remarkably than has ever been remembered."

In the course of his experiments upon the transpiration of plants, and their absorbing powers, Dr. HALES endeavoured, but always without success, to alter the flavour of their fruit by causing them to imbibe various perfumes. He placed a vessel upon a divided branch of a tree, so that it might absorb any fluid contained in it. Upon filling it with camphorated spirit of wine, the whole branch of an apple-tree was killed; but, though the apples hung several weeks afterwards, no alteration of taste was perceived in them, though the smell of camphor was strong in the leaf-stalks, and all other parts of the dead branch. Different perfumed waters were absorbed by fruit-trees without injuring them, but they failed to confer any peculiar flavour on the fruit.

If, as Dr. HALES' experiments seemed to show, the transpiration of plants, and the motion of the sap, as well as the absorption from the soil, depend upon the leaves, it became an interesting question to examine these points in evergreens; and he found that they absorbed less and transpired considerably less than other trees: hence, "the cedar of Libanus, and the ilex or evergreen oak, grafted on an English oak, and on a larch, were verdant all the Winter, though the leaves of the oak and larch decayed, and fell off as usual; the fact being, that evergreens live and thrive with very little nourishment."

Having proved that trees transpire large quantities of matter, our author next endeavoured to collect and examine it: he caused the branches and leaves to be enclosed in flasks and retorts; he placed a large sun-flower under the head of an alembic, and thus procured "what appeared to be pure water, very slightly tainted by vegetable matter; it seemed not to differ, though obtained from different plants." After some observations respecting the moisture and temperature of the earth, Dr. HALES proceeds with experiments to determine the force with which trees imbibe moisture, and here he obtained some striking results. He exposed the roots of a pear-tree, and cut off the end of one, half an inch diameter; the stump was cemented into the upper end of a tube twenty-six inches long, filled with water, and dipping at its lowest extremity into mercury. The root imbibed the water so vigorously, that in six minutes' time the mercury rose eight inches in the tube. This experiment was made in August. Another experiment, similarly contrived, in which a large branch of the root of an apple-tree was used, the diameter of its transverse section being three-fourths of an inch, caused the mercury to ascend five inches in half an hour. The oozing of air-bubbles from the cut surface interfered with the rise of the fluid in these tubes, but it was observed that the mercury rose highest when the sun was clear and warm; towards evening it subsided three or four inches, and rose again the next day. It also subsided during rain. This experiment was made in May. When we consider, says Dr. HALES, that the power thus required to raise mercury twelve inches, would raise water thirteen feet eight inches, we may form some idea of the power exerted by the growing vegetable.

Dr. HALES was one of the first who noticed the influence of cutting a ring of bark off the branch of a tree, (or *ringing*, as it is now technically called,) upon the growth of its fruit and leaves; but instead of attributing its effect to an accumulation of sap, the juice being prevented flowing downwards in the vessels of the bark, he refers it to a less quantity of sap arising, "whence it is better digested and prepared for the nourishment of the fruit;" he combats the notion of the sap *circulating* in trees, and imagines that it is often progressive at one time, and retrograde in another, in the same vessels.

Dr. HALES concludes his Vegetable Statics, with an account of some experiments to prove that a considerable quantity of air is inspired by plants, and with some observations on the growth of seeds and vegetables generally. By cementing a branch with its leaves, into a glass tube dipped into water, he observed the liquid rise in the tube, in consequence of the absorption of the confined air; and on putting a piece of the stem of a birch-tree under the receiver of an air-pump, he extracted abundance of air-bubbles from it during the exhaustion. He refers the first growth of a seed to the absorption of moisture, which swells it, and, as he thinks, protrudes nourishment into the radicle, which soon becomes capable of absorbing moisture from the soil; the root, he says, by expanding, carries the seed-lobes upwards with the plume, where they expand into leaves, which are of such importance to the tender plume, that it perishes on their removal; which renders it probable that they do the same office to the plume that the leaves adjoining to apples, quinces, and other fruits do to them; namely, draw the sap within reach of their attraction. As

the tree advances in stature the different lateral branches shoot out, "each lower order being longer than those immediately above them, not only on account of primogeniture, but also because, being inserted in larger parts of the trunk, and nearer the root, they have the advantage of being served with greater plenty of sap; hence arises the beautiful parabolical figure of trees. But when trees stand thick together in woods or groves, this their natural shape is altered, because the lower lateral branches being shaded, they can transpire little, and therefore drawing little nourishment, they perish; but the top branches being exposed to a free drying air, they transpire plentifully, and thereby drawing the sap to the top, they advance much in height; but if, when such a grove of tall trees is cut down, there be left here and there a single tree, that tree will then shoot out lateral branches; the leaves of which branches now transpiring freely, will attract plenty of sap, on which account the top, being deprived of its nourishment, usually dies."

Such are the leading objects of inquiry which engaged the attention of Dr. HALES; and, if we consider the little progress that had been previously made in pneumatic chemistry, we must allow that he much promoted that department of research: in his inquiries into the functions of vegetables he was at once original and acute, and laid the foundation of a very useful and curious series of investigations, which DUHAMEL, ANDREW KNIGHT, and others, have pursued with so much success. HALES entered into some collateral branches of investigation, the results of which are given in the *Philosophical Transactions*, and are collected in the second volume of his *Essays*; but they are not of such importance as to form any prominent feature in a general history of his discoveries.

When it is recollected that HALES wrote at the commencement of the last century, that there were then very few models of scientific composition extant that were worth copying, and that a pompous and obscure style of writing was prevalent among his experimental contemporaries, we cannot but admire the perspicuous and unadorned manner in which he details his facts and observations: he has all the merit that in this respect belongs to BOYLE, without his diffusiveness; and a pleasing vein of sound and unaffected morality accompanies his argument, and leads him, whilst endeavouring to unveil the mysteries of Nature, to direct our attention with becoming modesty to the penury of man's wisdom, when compared with the admirable adjustment of causes and effects discoverable in her lowliest works.

Contemporary with HALES was the celebrated HERMANN BOERHAAVE of Leyden, a man who laid medicine and chemistry under deep obligations; the former by his successful practice and happy method of instruction; the latter, by diligently experimenting in some of its most difficult departments. "He prosecuted chemistry," says Dr. JOHNSON, "with all the ardour of a philosopher whose industry was not to be wearied, and whose love of truth was too strong to suffer him to acquiesce in the report of others." BOERHAAVE's original chemical investigations were nearly of the same nature as those of HALES: he experimented upon the gaseous products afforded by a variety of vegetable and animal substances; he attributed the elasticity of air to its union with fire, and considered its ponderable matter as susceptible of chemical combinations. In disclosing

these views, he has certainly sketched an outline of one of the modern theories of combustion; but he went no further, and was not more successful than HALES, in discriminating between common air and the various gaseous products that resulted from some of his experiments. His writings are enumerated in chronological order, in the masterly sketch of his life, written by Dr. JOHNSON; "they have," says his biographer, "made all encomiums useless and vain, since no man can attentively peruse them without admiring the abilities and reverencing the virtues of the author." His only chemical work, entitled *Elementa Chemicæ*, was first published in 1732. It contains an useful essay on the History of the Science*.

§ IX.

THE names of BLACK and BERGMAN, with a host of others, either forgotten, or eclipsed by those eminent philosophers, occur in the division of our history at which we have now arrived, and which embraces its progress in the interval between the researches of HALES and those of PRIESTLEY. Chemistry now assumed a more important and interesting aspect: the facts already collected began to be digested and arranged, and active measures were taken to embody the scattered materials that presented themselves; to ascertain their relative value; to reject those which were unimportant or useless; and to select such as deserved to be dignified with the title of standard authorities. Dr. BLACK's researches possess a two-fold interest, for he not merely made important contributions to the facts of the science, but also established a new theory, connected with one of the most intricate of its subjects, heat.

Dr. JOSEPH BLACK was sprung from a Scottish family, transplanted first to Ireland and then to France, where he was born in 1728, on the banks of the Garonne. When twelve years of age, he was sent for edu-

* Boerhaave was born in December, 1668, at a village near Leyden. He died in September, 1738. He was an eminent ornament of medicine, as well as of chemical science. His oration upon resigning the office of Governor of the University of Leyden has been justly eulogized by Johnson. (*Life of Boerhaave*.) "He here declares in the strongest terms (says his eloquent biographer) in favour of experimental knowledge, and reflects with just severity upon those arrogant philosophers, who are too easily disgusted with the slow methods of obtaining true notions by frequent experiments, and who, possessed with too high an opinion of their own abilities, rather choose to consult their own imaginations than inquire into nature, and are better pleased with the charming amusement of forming hypotheses than the toilsome drudgery of making observations.

"The emptiness and uncertainty of all those systems, whether venerable for

their antiquity, or agreeable for their novelty, he has evidently shown; and not only declared, but proved, that we are entirely ignorant of the principles of things, and that all the knowledge we have is of such qualities alone as are discoverable by experience, or such as may be deduced from them by mathematical demonstration."

Boerhaave's contributions to physic were large and valuable. His *Elementa Chemicæ*, of which a good translation, with notes, was edited in 1753 by Dr. Shaw, he dedicated to his brother, who was intended for the medical profession, but went into the church; while Boerhaave, who originally studied divinity, relinquished it for physic and chemistry. Alluding to this circumstance, "Providence," says he, "has changed our views, and consigned you to religious duties, while I whose talents were unequal to higher objects, am humbly content with the profession of physic."

cation to Belfast, and afterwards to the University of Glasgow, where he entered upon the study of Physic, under the guidance of that bright ornament of medical science, Dr. WILLIAM CULLEN. In 1750, he removed to Edinburgh; four years afterwards, he took the degree of Doctor of Physic; and, in 1756, published his *Experiments on Magnesia, Quicklime, and some other alkaline substances, in the Physical and Literary Essays*. In the same year, CULLEN having removed to Edinburgh, BLACK returned to Glasgow, to fill the medical and chemical chair of that University, where he was received with open arms both by the classes and professors. In 1764, he brought his ideas respecting the combinations of heat with ponderable matter to maturity. Speculations upon this subject had occupied his mind during a considerable period, but the difficulties of the inquiry, and the time necessarily consumed in other professional avocations, had considerably interfered with the pursuit. In 1766, he was appointed to the chemical chair of Edinburgh, an office which he filled with such talent, industry, and perseverance, as not only drew an immense concourse of hearers to his class, but tended to confer upon chemistry a degree of popularity and importance, which has been greatly conducive to its promotion and extension. "His discourse," says his biographer, Professor ROBISON, "was so plain and perspicuous, his illustrations by experiment so apposite, that his sentiments on any subject never could be mistaken; and his instructions were so clear of all hypothesis or conjecture, that the hearer rested on his conclusions with a confidence scarcely exceeded in matters of his own experience*." In short, Dr. BLACK, in his professorial capacity, was entitled to every praise, and he contributed most essentially to the foundation and increase of the reputation which the University of Edinburgh has acquired and maintained. Nor was his private character at variance with his public excellence; he was mild, amiable, and fond of conversation, whether serious or sportive; and united to the highest philosophical attainments most of the elegant accomplishments of life. In his advanced age he often expressed a hope that he might not linger in protracted sickness, on account of the distress which, in such cases, is suffered by attending friends; and

* Dr. Black's character as a lecturer is given by his friend Professor Robison in the following terms:—"He endeavoured every year to render his courses more plain and familiar, and to illustrate them by a greater variety of examples in the way of experiments. No man could perform these more neatly and successfully. They were always ingeniously and judiciously contrived, clearly establishing the point in view, and never more than sufficed for this purpose. While he scorned the quackery of a showman, the simplicity, neatness, and elegance with which they were performed were truly admirable. Indeed, the *simplex munditiis* stamped everything that he did. I think it was the unperceived operation of this impression

that made Dr. Black's lectures such a treat to all his scholars. They were not only instructed, but (they knew not how) delighted; and without any effort to please, but solely by the natural emanation of a gentle and elegant mind, co-operating indeed with a most perspicuous exhibition of his sentiments, Dr. Black became a favourite lecturer; and many were induced, by the report of his students, to attend his courses, without having any particular relish for chemical knowledge, but merely in order to be pleased. This, however, contributed greatly to the extending the knowledge of Chemistry, and it became a fashionable part of the accomplishments of a gentleman."—*Preface*, p. LI.

his death, which happened in his seventy-first year, in November, 1799, is on this account the more remarkable. He was taking some milk and water, and having the cup in his hand, when the last stroke of his pulse was to be given, had set it upon his knee, and in this attitude expired without the smallest agitation.

The writings of BLACK, though few, are masterpieces of scientific composition. Newton was his model, and he was the first who transferred into chemistry the severe system of inductive logic, which marks the productions of that great master. "In no scientific inquiries, since the date of the *Principia* and *Optics*, do we find so great a proportion of pure ratiocination, founded upon the description of common facts, but leading to the most unexpected and important results, as in the two grand systems of BLACK." Averse to all hypothesis, and aware of the multitudinous facts upon which a theory that is to stand firm must be founded, Dr. BLACK was unwarrantably slow in the formal public disclosure of his researches. His tenets were fully and freely delivered to his pupils; but he rarely intruded upon the public as an author; and his achievements in the philosophy of heat are chiefly developed in his posthumous works. This silence, arising out of an overcautious modesty which marked all his proceedings, was not favourable to the reputation of Dr. BLACK. Faulty and incomplete copies of his lectures were circulated among his friends and admirers, which afterwards reached the hands of those who deserved another name, and by whom they were not very honourably employed.

When BLACK first entered the precincts of chemistry, there was a busy and acute controversy respecting the cause of causticity in earths and alkalis; it was supposed by STAHL that the conversion of limestone into quicklime depended upon its absorbing certain igneous particles; by MACQUER*, MEYER†, and others, the change was referred to an acrid

* Macquer was born at Paris in 1718, and died in 1784. He ranks among the most eminent scientific chemists of the early part of the eighteenth century; and though involved in the errors of the Phlogistic school, he has written with much good sense and perspicuity on a variety of chemical subjects. His most celebrated works are, the *Elemens de Chimie Théorique*, Paris, 1749; and *Elemens de Chimie Pratique*, Paris, 1751. He also published a Chemical Dictionary. The following is all his information respecting the property possessed by quicklime of rendering the alkalis caustic. After describing the process, he observes, "Le but de cette opération, est de réunir avec le sel alcali fixé ce que la chaux a de salin et d'âcre."—"On le combine avec la partie la plus âcre, la plus subtile, et la plus saline de la chaux."—"Nous n'entreprendrons point ici d'expliquer pourquoi le sel alcali, que l'on combine avec la chaux, acquiert une si grande causticité. Cette question nous paroît une des plus délicates et des plus difficiles à résoudre que nous

offre la Chimie. Elle tient à celle des propriétés alcalines de la chaux, et on ne peut guères espérer de la résoudre, que quand on aura acquis sur la nature de cette substance, beaucoup plus de lumières que nous n'en avons à présent."—*Elemens de Chimie Pratique*, pp. 179, 180.

† J. F. MEYER'S *Chemische versuche zur nähern erkenntniss des ungelöschten kalks; der elastischen und electrischen Materie, des allerreinsten feuerwesens, und der ursprünglichen allgemeinen saure*. Hanover, 1764. In this dissertation, though published subsequently to Black's essay, the causticity of the alkalis and lime is referred to the absorption of a principle which the author calls *Causiticum*, or *Acidum pingue*. Between the years 1760 and 1772, a great variety of dissertations were published in Germany upon this question, some in support of Black's doctrine, others in favour of Meyer's hypothetical absurdities. See GREN'S *Systematisches Handbuch der Gesammten Chemie*. Halle, 1794. § 437. —*Observ. Phys. Chem.*, 1722.

acid, contracted in the fire; by others, to nondescript saline particles. Dr. BLACK's notice appears to have been drawn to this inquiry, by the researches of HOFFMAN* concerning the nature of magnesia: he found that when that earth was obtained by adding a mild alkali to solution of Epsom salt, it effervesced upon the addition of an acid; but that if heated red-hot, it no longer effervesced, and moreover lost considerably in weight. The same fact applied equally to lime, and led him to believe, that that substance, instead of acquiring its acrimony by the absorption of something from the fire, became caustic by the loss or expulsion of one of its elements, in consequence of being heated. He then distilled some magnesia in a retort; but finding that, though it diminished considerably in weight, the only visible loss it sustained was a minute portion of water, he conceived the possibility of the escape of some gaseous matter; and, on mixing common magnesia and an acid in a proper phial, he collected a considerable quantity of a permanently elastic gaseous body: from chalk or limestone, and from the mild alkalis, he procured a similar gas, and he termed it *fixed air*.

In 1764, Dr. MACBRIDE, of Dublin, verified and extended these researches; he found that quicklime, after having been exposed to air, acquired the property of effervescing, and, consequently, fixed air must exist in the atmosphere†. He also explained the agency of lime as a manure, and introduced some important improvements into the art of tanning.

In 1765, Dr. BROWNRIGG threw out some curious hints upon the same subject: in a communication to the Royal Society, printed in the *Transactions* for that year, he remarks, "that a more intimate acquaintance with those noxious airs in mines, called *damps*, might lead to a discovery of that subtile principle of mineral waters, known by the name of their *spirit*; that the mephitic exhalations, termed *choak-damp*, he had found to be a fluid permanently elastic; and that, from various experiments, he had reason to conclude that it entered the waters of Pyrmont, Spa, and others, imparting to them that pungent taste, whence they are called *acidulæ*, and likewise that volatile principle on which their virtues chiefly depend;" and in 1760, Mr. LANE remarked the solubility of iron in water impregnated with fixed air.

I shall again have occasion to revert to the nature and properties of *fixed air*, which engaged much of the attention of PRIESTLEY, LAVOISIER, and other celebrated men, whose labours are yet to be noticed, consequently we may proceed to BLACK's researches on the subject of heat; researches which are more exclusively his own, and in which he has

* Hoffman was the most celebrated Chemical Physician of the age. He was born at Halle in Saxony, in 1660, and died in 1742. His writings, which are voluminous, are also valuable. In 1749, they were eked out by the Genevese booksellers into nine folio volumes. The following are his leading Essays in Chemistry: *Dissertationes de Generatione Salium*,—*De Natura Nitri*,—*De Cinabare Antimonii*,—*De Mirabili Sulphuris*

Antimonii fixati efficacia,—*De Mercurio et Medicamentis Mercurialibus*. *Observationum Physico-Chemicarum*—*Collectio*. Libri iii.

† MACBRIDE's *Experimental Essays*, 1764. The merit of this performance induced the University of Glasgow to bestow the degree of Doctor of Physic on the author. He was born in the county of Antrim in 1726, and died in 1778.

displayed that acuteness and originality which have given his name so high a rank in the annals of chemical science.

In speaking of the experiments of BOYLE, and of the investigations of the Florentine Academicians, two curious circumstances respecting the temperature of thawing ice and boiling water were noticed. It was stated that ice, during its liquifaction, retained an uniform temperature of 32° ; and that water, during its ordinary ebullition, never became hotter than 212° ; hence the use of those fixed points in the graduation of thermometers. We have now to examine the views which these phenomena suggested to Dr. BLACK, and the results that followed his inquiries into their causes and effects.

If a vessel of ice, of any very low temperature, be brought into a warm room, or placed near the fire, or over a small steadily burning lamp, a thermometer placed in it will gradually rise to 32° in the contact of the ice, and not higher, until the whole is melted. Then the temperature of the ice-cold water will begin to rise, and if the lamp be continued under the vessel, it will go on rising till it attains the temperature of 212° , when it again becomes stationary, and remains so during the whole evaporation. It follows, therefore, that heat is concerned in producing two series of changes: That its first effect is to thaw the ice without elevating the temperature; and that it then raises the thermometer till ebullition takes place, after which it converts the water into vapour, without elevating either its temperature or that of the vapour. Hence the following particular heads of inquiry suggested themselves:—

1. As to the *absorption* of heat during the conversion of solids into liquids, and of liquids into vapours.
2. As to the *evolution* of heat during the converse changes; namely, the condensation of vapours, and congelation of liquids.
3. As to the *quantity* of thermometric heat absorbed and evolved in these different cases.

The disappearance of thermometric or sensible heat alluded to in thawing ice, takes place in all corresponding cases of liquifaction; consequently, if a cold solid be mixed with a given weight of the same substance hot, and in a liquid state, the resulting temperature will not be the mean, as would have been the case if both portions had been in the liquid state, but will be considerably below it, a portion of the heat of the hotter body having been, as it were, consumed in liquifying the solid, without affecting its temperature. Thus equal parts of water at 212° and at 32° , give on mixture the mean temperature of 122° . But equal parts of water at 212° , and of snow at 32° , give upon mixture a temperature of 52° only, the excess of heat in this instance being concerned in *liquifaction*, not in elevation of temperature. Dr. BLACK considered the lost heat as equivalent to about 140° in the case of the liquifaction of ice; and among his experiments illustrative of this subject, the following may be selected as most relevant and simple:—Two similar globular glass vessels were filled with water, which in one was afterwards frozen; and in the other cooled as nearly as possible to the same point; they were then carried into a room of a temperature of 47° , there being no other difference between them than that the one contained ice and the other water. In half an hour the vessel of water had acquired the temperature of 40° ; but in the other it required ten hours and a half

to melt the ice, and raise the water to 40° . Now, as the access of heat was the same in both cases, and as this was at the rate of 7° in half an hour, it follows that in twenty-one half hours, (the time required to thaw the ice and elevate the temperature of the water to 40° ,) it would have received $7 \times 21 = 147^{\circ}$. The difference, therefore, between the increase of temperature in the ice and water vessels, with equal accessions of heat, is 140° , which will express the quantity of sensible heat rendered latent by the operation of liquifaction.

As heat is thus required to convert solids into liquids, it follows, that in cases of sudden liquifaction cold will ensue; hence its production, during the solution of many saline bodies, and hence, too, the explication of the theory of freezing mixtures. And as liquifaction is a cooling process, so congelation is a process in which heat is evolved. The freezing of large masses of water is actually a heating process to the circumjacent air. In the sudden crystallization of some saline solutions heat is evolved; and water, under certain circumstances, cooled to eight or ten degrees below its freezing point, suddenly rises to 32° upon congelation.

Having thus perspicuously disposed of the theory of congelation and liquifaction, Dr. BLACK turned his observation to the phenomena attendant on the formation of vapour, and there he was equally happy in his inquiries*.

When water is made to boil, the steam which rises from it is not hotter than the water itself, although there be a continuous influx of heat, which therefore must become *latent* in the steam; and consequently steam and other vapours may be regarded as compounds of liquids and heat.

To ascertain the thermometrical expression of the latent heat of

* "When we heat a large quantity of a fluid in a vessel, in the ordinary manner, by setting it on fire, we have an opportunity of observing some other phenomena which are very instructive. The fluid is gradually heated, and at last attains that temperature which it cannot pass without putting on the form of vapour. In these circumstances, we always observe that it is thrown into the violent agitation which we call boiling. This agitation continues as long as we throw in more heat, or any of the fluid remains, and its violence is proportional to the celerity with which the heat is supplied. Another peculiarity attends this boiling of fluids, which, when first observed, was thought very surprising. However long and violently we boil a fluid, we cannot make it in the least hotter than when it began to boil. The thermometer always points at the same degree, namely, the vaporific point of that fluid. Hence the vaporific point of fluids is often called their boiling point. When these facts and appearances were first observed, they seemed surprising,

and different opinions were formed with respect to the causes upon which they depend. Some thought that this agitation was occasioned by that part of the heat, which was more than the water was capable of receiving, and which forced its way through, so as to occasion the agitation of boiling; others, again, imagined that the agitation proceeded from air, which water is known to contain, and which is now expelled by the heat. Neither of these accounts, however, is just or satisfactory; the first is repugnant to all our experience in regard to heat: we have never observed it in the form of an expansive fluid like air; it pervades all bodies, and cannot be confined by any vessel, or any sort of matter; whereas, the elastic matter of boiling water, can be confined by external pressure, as is evident in the experiments made with Papin's digester."

This quotation from BLACK's *Lectures* (vol. i., p. 153) is inserted to show the state of the argument respecting the phenomena of ebullition previous to his researches.

steam, Dr. BLACK proceeded thus: The time required to elevate a quantity of water to its boiling point was carefully noted; the same heat was then continued till the whole had evaporated, and the time required also noted. Thus, supposing the accession of heat to have gone on above 212° , in the same ratio as below it, the temperature that the water would have acquired was estimated, whence it was inferred that the loss of sensible or thermometric heat amounted to more than 800° .

The vast evolution of heat during the condensation of steam now admitted of an explanation, and, on estimating the latent heat of steam, by condensing a given quantity in a given weight of water, it appeared to amount to between 900° and 1000° .

About the year 1774 it was observed by CULLEN* that a thermometer, moistened with spirit of wine or ether, sinks many degrees during the evaporation of those fluids: with ether, the thermometer may be made to fall from 60° to 0° . The cause of this is sufficiently explained by BLACK's theory; the ether and spirit readily pass into vapour, which requires a certain quantity of heat for its production: this is taken from the bodies it happens to be in contact with, as from the thermometer, or the hand; hence the cold perceived when these fluids are applied to the body, and the advantage which results from their application in cases of burns and inflammations. These circumstances led CULLEN to accelerate the evaporation of these fluids, by exposing them under the receiver of the air-pump: by placing a flask half full of ether in a tumbler of water, it was found that, during the process of exhaustion, the evaporation was so rapid from the ether in the flask, as to convert part of the surrounding water into ice†.

* "The chemistry of Stahl, as it was cultivated in Germany, and France, and other countries of Europe, scarcely aspired beyond the bounds within which it had been circumscribed by its original founder. A few important facts, indeed, were added, but they were either connected with medical preparations, or attracted attention solely as objects of curiosity. The great and tempting field of Philosophical Chemistry lay unexplored, when it was entered upon with ardour by Dr. Cullen, who first perceived its value, and whose genius and industry, had they not been turned into another channel, would, in all probability, have been crowned with the richest discoveries. But, though Dr. Cullen soon abandoned his chemical pursuits for those of medicine, he was fortunate enough to have initiated into the science a man whose discoveries formed an era in chemistry, and who first struck out a new and brilliant path, which was afterwards fully laid open, and traversed with so much eclat by the British philosophers who followed his career. This fortunate pupil of Dr. Cullen was Dr.

Joseph Black."—THOMSON, *History of the Royal Society*, p. 468.

Dr. Cullen's fame as a promoter of chemistry has been lost in his greater celebrity as a teacher of medicine. "Chemistry," says his biographer, Dr. Anderson, "which was, before his time, a most disgusting pursuit, was, by him, rendered a study so pleasing, so easy, and so attractive, that it is now pursued by numbers as an agreeable recreation, who, but for the lights that were thrown upon it by Cullen and his pupils, would never have thought of engaging in it at all."

Cullen was born in Lanarkshire, in 1712, and died at Edinburgh in 1790.

† Dr. Cullen's paper is published in the *Physical and Literary Essays and Observations*, Edinburgh, 1756, vol. ii. It contains the details of many interesting experiments upon the production of cold, and he considers the power of fluids in this respect as nearly according to the degree of volatility in each. "If to this," says he, "we join the consideration that the cold is made greater by whatever hastens the evaporation, and

The cause of the cold thus produced by evaporation now therefore became apparent, since no vapour can be in any instance formed without a proportionate absorption, or disappearance, of heat; and the theory of cooling by evaporation from surfaces, as in wine and water coolers composed of porous materials, and of cooling by the affusion of spirit of wine, ether, and other rapidly evaporating substances, became at once evident. LESLIE'S experiment on the production of ice by the evaporation of water *in vacuo*, and WOLLASTON'S *Cryophorus*, beautifully illustrate these views, but it would require much more extensive consideration than we can here afford, to trace all the bearings of the highly important investigations in which the name of BLACK is concerned. There is, however, one subject connected with them, upon which it would be improper not to offer one or two remarks: Dr. BLACK, in his published Letters, has said, "I have the pleasure of thinking, that the knowledge we have acquired concerning the nature of elastic vapour, in consequence of my fortunate observation of what happens in its formation and condensation, has contributed in no inconsiderable degree, to the public good, by *suggesting* to my friend Mr. WATT* of Birmingham, then of Glasgow, his improvements on this engine:" meaning the steam-engine, of which he is then speaking. We are not, however, to conclude from these lines that Dr. BLACK meant to assume any of the merit which exclusively and justly belongs to Mr. WATT; for in the context, he gives him all praise for the originality of his invention; and, in his private correspondence, recommends him particularly to assert, clearly and fully, his sole right to the honour of the improvements of the steam-engine; and, further, in a written testimonial given by Dr. BLACK to Mr. WATT, on the occasion of a trial at law in 1797, connected with a piracy of one of his inventions, after giving a brief account of it, he adds, "Mr. WATT was the sole inventor of the capital improvement and contrivance above-mentioned†."

particularly that the sinking of the thermometer is greater, as the air in which the experiment is made is warmer, if dry at the same time, I think we may now conclude that the cold produced is the effect of evaporation."

* The celebrated James Watt was born at Greenock, on the 19th of January, 1736; and died on the 25th of August, 1819, at Heathfield, near Birmingham, in the 84th year of his age.

† This may be the proper place to show in what way the views of Dr. BLACK'S *Theory of Latent Heat* are connected with the improvements of the steam-engine, a subject upon which I must necessarily be brief, as only in part belonging to the object of this history. The Marquess of Worcester is commonly regarded as the inventor of the steam-engine, but his claims are not well authenticated. It is true, that, among the Utopian schemes to be found in his *Century of Inventions*, there is a dark

description of a method of raising water by steam; but we can scarcely see how this was effected, nor are there any data recorded of the success of the contrivance. Be this as it may, he who barely and obscurely hints the possibility of an undertaking, cannot be regarded as forestalling him who successfully carries it into execution; and the first person who, upon decided evidence, constructed an engine for raising water by the alternate force and condensation of steam, was Captain Savary,—who also published an account of his invention in a small tract called the *Miner's Friend*. To enter into a description of this instrument would be irrelative to my present purpose; I, therefore, pass on to that of Newcomen, who, in 1705, obtained a patent for an improved steam-engine. It consisted of a boiler, having a cylinder placed upon it, in which was a solid plunger, connected by its rod with a beam and lifting-pump. The plunger

WATT's *capital improvement*, above alluded to, consisted chiefly in condensing in a separate vessel, and was adopted before he had any clear notion of Dr. BLACK's investigations; or at least the main experiments upon which this improvement hinged were previously undertaken.

was elevated by the elastic force of steam admitted from the boiler. The steam-cock being closed, a small stream of cold water was suffered to run into the cylinder, by which the steam was condensed; the pressure of the atmosphere then acting upon the surface of the plunger, forced it to the bottom of the cylinder, whence it was again raised by the re-admission of steam, and so on. In 1717, Mr. Henry Beighton became an improver of the steam-engine; he was probably the first who caused the steam-cock to be opened and shut by the machinery; for a man was obliged to attend Newcomen's engine for this express purpose. A few other improvements were made by different persons, but they did not affect the general action of the engine; the steam was alternately admitted into, and condensed in the main cylinder; and although defects in its power had been noticed, their cause was unknown until 1765, when, happily for the prosperity of the arts and manufactures of this country, the subject engaged the keen ingenuity of Mr. Watt. The model of a Newcomen's engine fell into his hands to be repaired, and in this he presently observed the immense loss of steam occasioned by its admission into the cylinder just cooled for condensation; indeed, he went so far as to ascertain, by experiment, that half the steam of the boiler was thus lost. For, having constructed a boiler which showed the quantity of steam expended at every stroke of the engine, he found that it many times exceeded that which was sufficient to fill the cylinder. But the circumstance that excited his greatest surprise was, that the injection water gained infinitely more heat than if a quantity of boiling water, equal to that required to form the steam, had been added to it. It was probably in this dilemma that he consulted Dr. Black; and the explanation of the difficulty will be obvious from the facts detailed in the text. To avail, himself, therefore, of the whole power of the steam, it became absolutely necessary to keep up the temperature of the cylinder constantly at the boiling point of water; this he was enabled to attain, by connecting with it

another vessel exhausted of air, and, immersed in cold water, into which, when communicated with the cylinder, the steam, being an elastic fluid, instantly rushes and is condensed; and, on closing its connexion with the cylinder, the steam again admitted there now operates with full force, and suffers no further condensation. To carry off the water from the second vessel, which he calls the *condenser*, and to perpetuate the vacuum, Mr. Watt attached to it a pump, by which both the air and condensed water are removed. The engine thus altered produced the same power as one of equal dimensions on Newcomen's plan, with rather less than one third the quantity of steam; hence was a considerable hindrance to the use of the engine materially diminished, namely, the expense of fuel.

But great as was this improvement, it forms a small part of the successful achievements of Mr. Watt in this department of mechanics; he amended the apparatus for boring the cylinders, and improved every part of the working gear of the engine; and he infinitely extended its applications and utility, by applying the power of steam to produce motion round an axis; but their enumeration would lead me out of the bounds of chemistry. I, therefore, hasten to the invention which may be said to have perfected the steam-engine. Steam had hitherto only been used to force the piston down,—it was returned by a weight attached to the other end of the beam. Mr. Watt, in 1782, constructed an engine in which steam was used to elevate as well as to depress the piston, an alternate vacuum being formed above and below it, by the condenser, as before. An engine upon this plan, executed at Mr. Watt's manufactory, at Soho, near Birmingham, was first employed at the Albion Mills, near Blackfriar's-bridge, London, in 1788.

An excellent sketch of the history of the steam-engine will be found in the *Edinburgh Review*, vol. xiii. p. 311, and some valuable additions to the biography of Watt and the history of his discoveries are contained in the *Eloge* of M. ARAGO.

It must be observed here, that Mr. WATT made a variety of curious investigations upon the subject of steam, and of the capacity of bodies for heat (a subject first inquired into by Dr. BLACK, in 1762), in themselves highly important: but these, and his other mechanical and chemical researches, have been obscured by the magnitude of his inventions and discoveries more immediately connected with the perfection of the steam-engine.

If the suspicion of jealousy, of want of candour, or of any deviation from the strictest veracity, could, by any possibility, attach to either of the philosophers whose labours we have been adverting to, it might be worth entering into such details as would more distinctly unfold their respective claims; as it is, however, I trust the short allusion made to the subject, while it places the assertions of the one in their proper light, will sufficiently vindicate the exalted merit and indisputable originality of the other.

To Mr. WATT's character, in relation to the public, and as a private individual, it is more than difficult to do justice, for the combined eloquence of the different writers who have attempted it has only feebly depicted the influence of his talents upon the state of society; and still less has it succeeded in the more difficult portraiture of the man, occupied in the ordinary duties of life, and in the intercourse of social converse. Such, at least, is my impression upon looking over the different biographical sketches that have lately appeared. I consider myself as highly fortunate in having occasionally enjoyed the society, and profited by the information of one who was so eminent a benefactor to his country. "He was a man," says Sir WALTER SCOTT, "whose genius discovered the means of multiplying our national resources to a degree, perhaps even beyond his own stupendous powers of calculation and combination; bringing the treasures of the abyss to the surface of the earth; giving the feeble arm of man the momentum of an Afrite; commanding manufactures to arise, as the rod of the Prophet produced water in the desert; affording the means of dispensing with that time and tide which wait for no man, and of sailing without that wind which defied the commands and threats of Xerxes himself. This potent commander of the elements,—this abridger of time and space,—this magician, whose cloudy machinery has produced a change on the world, the effects of which, extraordinary as they are, are perhaps only now beginning to be felt, was not only the most profound man of science, the most successful combiner of powers and calculator of numbers, as adapted to practical purposes; was not only one of the most generally well-informed, but one of the best and kindest of human beings. In his eighty-fourth year his attention was at every one's question, his information at every one's command." "No individual in his age," says another, and equally able writer, "possessed more varied and exact information. He had infinite quickness of apprehension, a prodigious memory, and a certain rectifying and methodizing power of understanding, which extracted something precious out of all that was presented to it. His stores of miscellaneous knowledge were immense, and yet, less astonishing than the command he had over them. His conversation had all the charms of familiarity, with all the substantial treasures of knowledge. With this philosophical

excellence of character, be it never forgotten that Mr. WATT conjoined the higher duties and more exalted attributes of sincere, but unaffected piety. Expressing his gratitude to Providence for that length of days and exemption from infirmity which rendered the evening of his life cheerful and serene, he yielded up his soul in the calmest tranquillity, and passed, without pang or struggle, from the bosom of his family to that of his God!"

§ X.

It is not perfectly in chronological order, to proceed in the present Section to the discoveries of Dr. PRIESTLEY*, and yet they are so numerous and important, that it will be difficult to continue the history of chemistry up to his time, without allusion to their objects and results. I shall, therefore, endeavour to give the reader some insight into the nature and bearings of his inquiries.

PRIESTLEY'S entire force was directed upon Pneumatic Chemistry. We have seen what may be termed the materials for the foundation of this branch of knowledge, in the works of MAYOW and HOOKE; it was pursued, as we have also found, with much diligence, but, unfortunately, in rather a desultory style, by HALES; PRIESTLEY directed his attention to it with a degree of activity and skill peculiarly his own; and, in the number of his discoveries, left his contemporaries far in the back-ground, while he certainly rivalled them in their interest and importance; and this is the more surprising, when we reflect that his philosophical studies seem generally to have been considered as subordinate to more severe and serious occupations. He first turned his attention to chemistry about 1768; he used to amuse himself with experiments on fixed air and artificial mineral waters, and one experiment, as he says, leading to another, he soon collected those materials which he laid before the Royal Society in 1772, under the title of *Observations on different Kinds of Air*. With what zeal and success he prosecuted this subject, will be seen in the sequel.

The apparatus which is now used in the chemistry of gaseous bodies, is almost entirely of PRIESTLEY'S invention. The water-trough, with its sliding shelves and moveable supports for inverted jars; the methods of subjecting animals and plants to the action of different kinds of air; the mercurio-pneumatic apparatus for collecting gases absorbable by water; the means of measuring and weighing gases, and of subjecting them to the action of electricity, are only a few of the contrivances for which we are principally indebted to PRIESTLEY; many others, employed by MAYOW and HALES, were by him perfected or improved.

In his earliest experiments on fixed air, and on air tainted by combustion and respiration, Dr. PRIESTLEY has announced many highly interesting and new facts; but the discovery which takes precedence of the others, and upon which his fame has been chiefly, though not quite justly, founded, is that of Oxygen Gas, or, as he termed it, Dephlogisticated Air. I say not quite justly, because its brilliancy and importance have been suffered to overshadow many of his other original investigations, of

* Born at Fieldhead, near Leeds, 1733; died in Pennsylvania, 1804.

which we hear but little, though their aggregate influence upon the subsequent progress of chemistry was most direct and important; but the fact is, that PRIESTLEY having opened, as it were, a new and rich mine in the science, found therein such abundance of treasure, that he was able to do little more than bring it to the surface, where it was soon pillaged and carried off.

Dephlogisticated Air was discovered by Dr. PRIESTLEY on the 1st of August, 1774; the method of experimenting which he adopted, consisted in exposing a quantity of *Red Precipitate of Mercury* to the action of the sun's rays concentrated by a burning lens; the red precipitate was contained in a small flask, filled up with quicksilver, and inverted in a basin of the same metal. "I presently found," he says, "that by means of this lens air was expelled from it very readily. Having got several times as much as the bulk of my materials, I admitted water to it, and found that it was not imbibed by it. But what surprised me more than I can well express, was, that a candle burned in this air with a remarkable vigorous flame, very much like that enlarged flame with which a candle burns in nitrous air exposed to iron or liver of sulphur; but, as I got nothing like this remarkable appearance from any kind of air besides this particular modification of nitrous air, and I knew no nitrous acid was used in the preparation of the *mercurius calcinatus*, I was utterly at a loss how to account for it*." Red Lead, and several other substances, among which is enumerated *Nitre*, are also shown by our author to afford oxygen at a red heat; and here we may revert to the sagacity displayed by HOOKE in his notions already quoted, respecting the constitution of that salt, and its nitro-aërial particles; and remind the reader how remarkably his surmises have been verified by PRIESTLEY; for, upon turning to those pages of the *Micrographia*, in which the theory of combustion is explained, we cannot but admire the penetration with which the presence of a body possessing the qualities of oxygen is anticipated, though the experimental demonstration of its existence was not achieved till the middle of the succeeding century. To MAYOW we might pay a similar tribute of applause; but, in canvassing the discoveries of LAVOISIER and his associates, a more favourable opportunity will offer of placing these matters in their true light.

The "nitrous air exposed to iron," alluded to in the preceding paragraph, is the gas now called Nitrous Oxide, which PRIESTLEY also discovered, though he but imperfectly investigated its properties.

The next remarkable circumstance adverted to by our author in

* The following paragraph, with which Dr. Priestley prefaces his account of the discovery of Dephlogisticated Air, presents a picture of his mind in regard to the origin of his own researches.

"The contents of this section will furnish a very striking illustration of the truth of a remark which I have more than once made in my philosophical writings, and which can hardly be too often repeated, as it tends greatly to encourage philosophical investigations; viz., that more is owing to what we call

chance, that is, philosophically speaking, to the observation of *events arising from unknown causes*, than to any proper design or preconceived *theory* in this business. This does not appear in the works of those who write *synthetically* upon these subjects, but would, I doubt not, appear very strikingly in those who are the most celebrated for their philosophical acumen, did they write *analytically* and ingenuously." (*Exp. and Obs.*, vol. ii., p. 103.)

respect to dephlogisticated air, is its action upon nitrous gas, mixed with which, "it occasioned a much more considerable diminution than atmospheric air;" and, as the fitness of air for respiration appeared connected with the absorption thus produced, it was inferred that it would support respiration, an inference which the Doctor soon verified by placing a mouse in a jar of the dephlogisticated air, in which it lived half an hour, though, by previous trials, he knew that it would only live a quarter of an hour in the same bulk of atmospheric air.

In the observations connected with these experiments, PRIESTLEY enters pretty much at length into the theory of the production of dephlogisticated air; but I shall not follow him into these views, as they are not very consistent with facts, nor even plausibly applied to them: he hints, however, at several useful applications of oxygen, and especially recommends it for the production of intense heat, by directing a small jet of it upon a piece of burning charcoal.

Among the many and ingenious investigations of this Philosopher, none have produced more pleasing subjects of inquiry than those relating to the influence of vegetation upon air contaminated by combustion, respiration, and the putrefaction of animal matter. Finding that air was not spoiled by the growth of a sprig of mint kept in it for some months, he thought it possible that the process of vegetation might restore the air injured by burning candles; and, accordingly, on the 17th of August, 1771, he put a sprig of mint into air in which a wax candle had burned out, and, on the 27th of the same month, found that another candle burned perfectly well in it; and then, to verify the conclusion, he divided the injured air into two separate portions, putting the plant into one of them, and merely leaving the other standing over water; he never failed to find that a candle would burn in the former, but not in the latter. "This restoration of air," says PRIESTLEY, "I found depended upon the vegetating state of the plant; for though I kept a great number of the fresh leaves of mint in a small quantity of air in which candles had burned out, and changed them frequently for a long space of time, I could perceive no melioration in the state of the air. This remarkable effect does not depend upon anything peculiar to *mint*, for I found a quantity of this kind of air to be perfectly restored by sprigs of *balm*." Groundsel, spinach, and some other plants, were used with like effect, to show that it did not depend upon aromatic effluvia. In Dr. PRIESTLEY's *Observations on Air infected with Animal Respiration and Putrefaction*, a multitude of other facts are adduced to demonstrate its renovation when exposed to growing vegetables, and he is thus led to the following general remarks upon the subject:—"These proofs of a partial restoration of air by plants in a state of vegetation, though in a confined and unnatural situation, cannot but render it highly probable, that the injury which is continually done to the atmosphere by the respiration of such a number of animals, and the putrefaction of such masses of both vegetable and animal matter, is, in part at least, repaired by the vegetable creation; and notwithstanding the prodigious mass of air that is corrupted daily by the above-mentioned causes, yet, if we consider the immense profusion of vegetables upon the face of the earth, growing in places suited to their nature, and, consequently, at full liberty to exert all their powers, both inhaling and

exhaling, it can hardly be thought but that it may be a sufficient counter-balance to it, and that the remedy is adequate to the evil*."

In the year 1778 Dr. PRIESTLEY resumed this investigation, and verified his main conclusions by new and satisfactory experiments; he found, however, that it was necessary for their success that the plants should be in a state of healthy and natural vegetation, and that all plants were not equally efficacious, some indeed appearing rather to deteriorate than improve the contaminated atmosphere. About this time, too, he made the capital discovery of the evolution of oxygen by aquatic plants, growing in water containing carbonic acid; that the presence of light was necessary to this change; that in sunshine it was most rapid; that it was in great measure independent of warmth; and, lastly, that the bladders of some kinds of sea-weed (*fucus vesiculosus*), often contained air purer than the atmosphere. The renovation of the air contained in water, requisite for the respiration of fishes, was thus accounted for; and the circumstance of fishes and most other aquatic animals being unable to live for any time in pure water, though exposed to air, satisfactorily explained.

By his contrivance of receiving gaseous fluids over quicksilver, PRIESTLEY was able to collect and examine a number of new æriform products, absorbable by water; and in these inquiries he was eminently successful. CAVENDISH, in endeavouring to get inflammable air from a mixture of copper and spirit of salt, obtained one that lost its elasticity on the contact of water. "I was exceedingly desirous," says PRIESTLEY, "to become acquainted with it, and therefore began by making the experiment in quicksilver, which I never failed to do in any case when I suspected that air might either be absorbed by water, or in any other manner affected by it: and, by this means, I presently got a much more distinct idea of the nature and effects of this curious solution." He then goes on to show that this singular gas is derived from the acid, that it is very absorbable by water, and that common Spirit of Salt is in fact an aqueous solution of it. His next discovery in this department was that of an alkaline air from a mixture of lime and sal-ammoniac; it also was absorbed by water forming "volatile spirit of sal-ammoniac, much stronger than that procured by any other means." He now thought that by adding the acid to the alkaline air, he might possibly produce a neutral air, but immediate condensation ensued, and sal-ammoniac was deposited. What is now termed Sulphurous Acid, (or by PRIESTLEY Vitriolic Acid Air,) he also discovered; he obtained it in various ways, but chiefly by heating mercury with oil of vitriol; he examined many of its combinations, and inquired into its action upon a variety of bodies†.

* PRIESTLEY on Air, vol. i. p. 93, 3rd edition, 1781.

† The notice of this discovery enables me, by the insertion of the following extract from his *History of Vitriolic Acid Air*, to show the candour and exactness with which he acknowledges the hints, assistance, and discoveries of others:—

"My first scheme was to endeavour to get the vitriolic acid in the form of

air, thinking that it would probably be easy to confine it by quicksilver, for, as to the nitrous acid, its affinity with quicksilver is so great that I despaired of being able to confine it to any purpose. I, therefore, wrote to my friend Mr. Lane to procure me a quantity of volatile vitriolic acid," &c. "Seeing Mr. Lane the winter following, he told me, that if I would only heat any oily or greasy

I have now enumerated the principal discoveries which PRIESTLEY may claim as original; and, in importance, they are second to none that had been previously made, and barely inferior to those that have adorned the later progress of chemistry. We can scarcely call him the founder of Pneumatic Chemistry, after perusing the works of HALES and BLACK; but he achieved more in that new department of the science than any of his predecessors or contemporaries; and though on some points anticipated, his claims to originality are on others quite unequivocal. He cannot be called the discoverer of Nitrous Gas, for it is noticed by MAYOW; yet he developed its principal properties, pointed out its useful eudiometrical applications, and showed many new modes of obtaining it. He has been stigmatized as a defender of the unintelligible system of phlogiston; and he did defend it with unpardonable pertinacity*; but when we reflect that equally erroneous theories have been as warmly espoused in our own

matter with oil of vitriol, I should certainly make the very thing I wanted, viz., the volatile or sulphureous vitriolic acid; and, accordingly I meant to have proceeded upon this hint, but was prevented from pursuing it by a variety of engagements.

"Some time after this I was in company with Lord Shelburne, at the seat of Mons. Trudaine, at Montigny, in France; where, with that generous and liberal spirit by which that nobleman is distinguished, he has a complete apparatus of philosophical instruments, with every other convenience and assistance for pursuing such philosophical inquiries as any of his numerous guests shall choose to entertain themselves with. In this agreeable retreat, I met with that eminent philosopher and chemist, Monsieur Montigni, Member of the Royal Academy of Sciences; and conversing with him upon the subject, he proposed our trying to convert oil of vitriol into vapour, by boiling it on a pan of charcoal in a cracked phial. This scheme not answering our purpose, he next proposed heating it together with oil of turpentine. According, we went to work upon it, and soon produced some kind of air, confined with quicksilver; but our recipient being overturned by the suddenness of the production of the air, we were not able to catch any more than the first produce, which was little else than the common air which had lodged on the surface of the liquor, and which appeared to be a little phlogisticated by its not being much affected by a mixture of nitrous air."

* Dr. Priestley's last publication is a tract, which appeared after his retirement to America, in 1800. It is entitled *The Doctrine of Phlogiston established, and*

that of the Composition of Water refuted.

It contains a variety of miscellaneous observations on the phlogistic and antiphlogistic theories, but it would be useless to follow the author into his unsubstantial speculations on these subjects. He has, however, thrown out some important considerations relating to his claims of originality as the discoverer of dephlogisticated air. The following paragraph appears of sufficient interest to be transcribed:—"Now that I am on the subject of the *right of discoveries*, I will, as the Spaniards say, leave no ink of this kind in my inkhorn; hoping it will be the last time that I shall have any occasion to trouble the public about it. M. Lavoisier says (*Elements of Chemistry, English translation*, p. 36), 'this species of air (meaning dephlogisticated) was discovered almost at the same time by Mr. Priestley, Mr. Scheele, and myself.' The case was this:—Having made the discovery some time before I was in Paris in 1774, I mentioned it at the table of M. Lavoisier, when most of the philosophical people in the city were present; saying, that it was a kind of air in which a candle burned much better than in common air, but I had not then given it any name. At this all the company, and M. and Madame Lavoisier as much as any, expressed great surprise; I told them I had gotten it from *precipitate per se*, and also from *red lead*. Speaking French very imperfectly, and being little acquainted with the terms of chemistry, I said *plomb rouge*, which was not understood till M. Macquer said, 'I must mean *minium*.' Mr. Scheele's discovery was certainly independent of mine, though I believe not made quite so early." P. 88.

days by men who in no respect are to be considered as inferior to our author, we must not impeach his discernment upon so flimsy an accusation. When we consider his numerous, and as it were, incompatible occupations; and remember the many channels into which his exertions were occasionally directed, we presently detect the source of that wavering of opinion and unsteadiness of research which his philosophical pursuits display. His experiments were almost always submitted to the public in a crude and undigested form, for he had no time to build them into theories, or to concoct them into generalizations; and it is perhaps as well that he had not, for the bent of his mind was evidently such as to shine in experiment rather than argument.

The constitution of the atmosphere was one of the many inquiries which engaged PRIESTLEY's diligence*. In 1772, Dr. RUTHERFORD demonstrated the existence of a peculiar elastic fluid in atmospheric air, differing from fixed or mephitic air, and yet, like it, extinguishing flame, and unfit for respiration†. This component part of the atmosphere was, by PRIESTLEY, called Phlogisticated Air; and he showed that when mixed with nitrous gas, it suffered no diminution; but, on the contrary, that dephlogisticated air, on the same admixture in due proportions, was almost entirely absorbed over water; hence the method before noticed which he introduced, of ascertaining what was termed the goodness of atmospheric air, by the degree of absorption exhibited upon a certain admixture of nitrous gas, over water.

It was for his various discoveries, and more especially those relating to the physiology of vegetation, that the Council of the Royal Society honoured Dr. PRIESTLEY by the presentation of Sir GODFREY COPLEY's medal, on the 30th of November, 1783‡.

* The ancients appear to have regarded air as an ultimate principle of matter. Thus Lucretius,—

Aera nunc igitur dicam, quid corpore toto
Innumerabiliter privis mutatur in horas:
Semper enim, quodquomque fluit de rebus, id omne
Aeris in magnum fertur mare, qui nisi contra
Corpora retribuat rebus, recreetque fluentis,
Omnia jam resoluta forent, et in aera versa,
Haud igitur cessat gigni de rebus, et in res
Recidere assidue, quoniam fluere omnia constat.

De Rerum Natura, Lib. V. v. 274.

† "Sed Aer salubris et purus, non modo respiratione animali ex parte fit mephiticus, sed et aliam indolis suæ mutationem inde patitur. Postquam enim omnis aer mephiticus ex eo, ope lixivii caustici secretus et abductus fuerit, qui tamen restat nullo modo salubrior inde evadit, nam quamvis nullam ex aqua calcis præcipationem faciet, haud minus quam antea, flammam et vitam extinguit."

‡ Sir Godfrey Copley originally bequeathed five guineas to be given at each anniversary meeting of the Royal Society, by the determination of the President and Council, to the person who had been the author of the best paper of

experimental observation for the year past. In process of time, this pecuniary reward, which could never be an important consideration to a man of enlarged and philosophical mind, however narrow his circumstances might be, was changed into the more liberal form of a gold medal, in which form it is become a truly honourable mark of distinction, and a just and laudable object of ambition. It was, no doubt, always usual with the Presidents, on the delivery of the medal, to pay some compliment to the gentleman on whom it was bestowed; but the custom of making a set speech on the occasion, and of entering into the history of that part of philosophy to which the experiment related, was first introduced by Mr. Martin Folkes. The discourses, however, which he and his successors delivered, were very short, and were only inserted in the minute-books of the Society; none of them had ever been printed before Sir John Pringle was raised to the chair of the Society.—CHALMERS's *Biographical Dictionary*.—*Life of Pringle*.

Sir JOHN PRINGLE, who was then President, delivered on this occasion an appropriate discourse upon the different kinds of air, in which, after expatiating upon the discoveries of his predecessors, he points out the especial merits of PRIESTLEY's investigations. In allusion to the purification of a tainted atmosphere by the growth of plants, the President has thus expressed himself:—

“From these discoveries we are assured that no vegetable grows in vain; but that, from the oak of the forest to the grass of the field, every individual plant is serviceable to mankind; if not always distinguished by some private virtue, yet making a part of the whole which cleanses and purifies our atmosphere. In this the fragrant rose and deadly nightshade co-operate; nor is the herbage, nor the woods that flourish in the most remote and unpeopled regions, unprofitable to us, nor we to them, considering how constantly the winds convey to them our vitiated air, for our relief and their nourishment. And if ever these salutary gales rise to storms and hurricanes, let us still trace and revere the ways of a beneficent Being, who not fortuitously, but with design, not in wrath, but in mercy, thus shakes the water and the air together, to bury in the deep those putrid and pestilential effluvia which the vegetables on the face of the earth had been insufficient to consume*.”

The chemistry of gaseous bodies, in consequence chiefly of PRIESTLEY's investigations, now became a main branch of the science, and some of his most eminent contemporaries were equally diligent with himself in its promotion and elucidation. Among others, BERGMAN and his friend and pupil, SCHEELE, may be ranked among its successful followers; and CAVENDISH lent it his powerful aid; but I have thought it better to confine myself to the abstract view of such of PRIESTLEY's discoveries as may

* Dr. Franklin, in a letter upon the subject of these discoveries to Dr. Priestley, has expressed himself as follows:—

“That the vegetable creation should restore the air which is spoiled by the animal part of it looks like a rational system, and seems to be of a piece with the rest. Thus, fire purifies water all the world over. It purifies it by distillation when it raises it in vapour, and lets it fall in rain; and further still by filtration, when keeping it fluid, it suffers that rain to percolate the earth. We knew before that putrid animal substances were converted into sweet vegetables when mixed with the earth and applied as manure; and now, it seems that the same putrid substances, mixed with the air, have a similar effect. The strong thriving state of your mint, in putrid air, seems to show that the air is mended by taking something from it, and not by adding to it. I hope this will give some check to the rage of destroying trees that grow near houses, which has accompanied our late improve-

ments in gardening, from an opinion of their being unwholesome. I am certain from long observation, that there is nothing unhealthy in the air of woods; for we Americans have everywhere our country habitations in the midst of woods, and no people on earth enjoy better health, or are more prolific.”—*Phil. Trans.* 1772, page 199.

Notwithstanding these researches, which have exposed some very curious facts relative to the chemical physiology of plants, it must be confessed that the causes of the renovation and equality of our atmosphere are yet by no means ascertained; for, although some growing vegetables do, under certain circumstances, purify the air (by the absorption of carbon and the evolution of oxygen), yet, when in a state of decay, they invariably add to its contamination; and a general view of the subject would lead us to [conclude that vegetables produce little effect upon the general constitution of the atmosphere.

be strictly termed his own, than to blend them with the achievements of other philosophers, who experimented with distinct views, though occasionally treading in his footsteps.

§ XI.

BERGMAN, of Sweden, was born in the year 1735, and died in 1784, in consequence of too intense application to his studies: he was not only a diligent traveller in the beaten paths of chemistry, but he searched the depths, and ascended the heights of the science; his life was short, but as he neither lost nor misemployed time, his activity compensated for the brevity of his days; he not only opened a new mine in his favourite science, but examined its treasures and scattered its riches, for BERGMAN may be said to have almost invented the art of chemical analysis.

In his *Prefatory Essay on the Investigation of Truth*, this author has depicted his feelings upon the subject of experimental science in perspicuous and unaffected terms; and a mind so directed could not but be successful in its exploits, when we remember that even in his days there were few willing entirely to throw off the presumption of scholastic philosophy. "A tendency," he says, "to Cartesianism still exists, and upon attentive consideration it will not appear wonderful that the human mind should delight to indulge in this method; for, on the one hand, the way of experiments is expensive, troublesome, and tedious; all minds, therefore, are not capable of enduring it; many are without the proper instruments, others want the necessary dexterity; but the most universal defect is that of patience and perseverance, so that if the experiment does not at once succeed it is abandoned in disgust. Man, in his ordinary state, seems by nature prone to indolence. On the other hand, the contemplative method favours the desire of knowledge; by pretending to unlock the secrets of nature with ease and expedition, it soothes the natural rage of explaining all things; and by supposing everything accessible to the human intellect, administers pleasing flattery to vanity and arrogance."

It is upon the talents of BERGMAN, as an analyst, that I propose to dwell; it is there that he was pre-eminently original and successful, and upon that foundation his character as a chemist may safely be built.

The use of tests, for the discovery of certain substances held in aqueous and other solutions, is first particularly dwelt upon by BOYLE, and he was sometimes very fortunate in their contrivance and applications. He noticed the conversion of certain vegetable blues to red by acids, and to green by alkalis; the cloudiness produced by common salt in solution of silver, its discoloration by liver of sulphur, and several other circumstances connected with the detection of certain principles by chemical re-agents. In 1667 DU CLOS undertook an examination of the waters of France; and in 1686 HIERNE published some clever experiments upon the same subject in Sweden. In these writers the use of galls for the detection of iron is alluded to, and the necessity pointed out of examining the residuary product of evaporation. In 1726 and 1729 BOULDUCE used spirit of wine to precipitate certain saline bodies insoluble in that menstruum. In 1755 VENEL pointed out the existence of fixed

air in the waters of Seltzer, Spa, and Pyrmont; LANE, in 1769*, showed the method of imitating chalybeate springs; and in 1772 Dr. PRIESTLEY published directions for saturating water with fixed air.

BERGMAN, in his *Essay on Mineral Waters*, after adverting to a variety of circumstances relating to their general characters and sources, proceeds to point out, in the seventh section, the principal re-agents and precipitants useful in their examination, and to describe the nature of their changes and indications, with useful precision, in the following order:—

A. Infusion of litmus, or turnsole, is so delicate a test for the acids, that a single grain of sulphuric acid reddens 408 cubic inches of the blue tincture. Paper, dipped in this tincture, and reddened by distilled vinegar, has its blue colour restored by alkalis; but the tincture is more sensible than the paper, for the latter is not reddened by ærial acid (fixed air); yet one part of water, saturated with ærial acid, renders fifty parts of the infusion red.

B. Tincture of Brazil-wood becomes blue by alkalis, and is sensible to less than one grain of crystallized soda in 4000 of water.

C. Turmeric, either on paper, or in watery tincture, is a good, but less sensible, test for alkalis, which render it brown.

D. Tincture of galls discovers iron by a purple or black cloud.

E. Prussiate of Potash produces a blue tinge in water containing a minute portion of iron; it also precipitates other metals; copper, brown; manganese, white.

F. Sulphuric acid forms a white precipitate in all solutions containing baryta. If it produces bubbles, it indicates some combination of ærial acid. Nitric acid is highly useful for showing the presence of sulphur, which it precipitates from hepatic waters.

G. Oxalic acid detects the minutest quantity of lime, by producing a white cloud, either immediately or after some hours. This test shows that scarcely any water is free from lime; and the purest, within twenty-four hours, deposits a portion of oxalate of lime, although sometimes so sparingly as to escape observation, unless lines be drawn on the bottom of the vessel with a glass rod, in the direction of which the precipitate attaches itself.

H. Aërated fixed alkali throws down the metals and earths; if the substance be easily soluble in ærial acid, the caustic alkali may be used.

I. Aërated volatile alkali also throws down earths and metals, and is an excellent test for the presence of copper, which it indicates by a blue colour, more or less intense according to the quantity of alkali added.

K. Lime-water detects ærial acid, by a precipitate of aërated lime.

L. Muriate of baryta forms an insoluble white precipitate in water containing any soluble vitriolic salt; twelve grains of crystallized Glauber's salt, dissolved in a kanne of distilled water (about three quarts), immediately exhibits white striæ on the application of this test. Even one grain in the kanne exhibits a white cloud after some hours, and as it only contains 0.26 grains of

* Mr. Lane was the first who ascertained the solubility of iron in water impregnated with fixed air.—*Phil. Trans.* 1769. "By this means," says Sir John Pringle, in his discourse on the different kinds of air, delivered at the anniversary meeting of the Royal Society, November 30, 1773, "the nature of the metallic

principle in mineral waters was clearly explained, and the whole analysis of those celebrated fountains, so often attempted by chemists and others, and still eluding their laboured researches, was thus, in the most simple manner, brought to light."

sulphuric acid, we may judge of the nicety of this precipitant, which even exceeds turnsole itself in sensibility. M. Muriate of lime may be used for the detection of fixed alkali, but it is an ambiguous test, because, if sulphate of magnesia be present, it produces gypsum. N. Solution of alum is also of little use, though occasionally employed as a test for alkalis. O. Nitrate of silver is a certain and delicate indicator of muriatic acid and its combinations. A grain of common salt, in a kanne of water, is instantly rendered evident by white streaks. Under some circumstances it may also form a precipitate with sulphuric acid, but sulphate of silver is much more soluble than Muriate; thus, no visible turbidness arises, unless the kanne of water contains ninety-eight grains of Glauber's salt, or twenty five of vitriolic acid. The presence of hepatic air renders the precipitate of silver more or less brown. Alkalis, lime, and magnesia, also precipitate nitrate of silver. P. Nitrate of mercury is a prevaricating test, but very sensible to a variety of substances that may exist in mineral waters. As BERGMAN has not pointed out any particular application, in which this salt is essential, it will not be necessary to follow up his remarks on it, though in other respects important. Q. Corrosive sublimate; R. Acetate of lead; S. Sulphate of iron; and T. White arsenic are enumerated, but their utility is dubious, and the observations upon them of little value to the analyst. U. Spirituous solution of soap is useful in giving general indications of the purity of water, which, if pure, scarcely renders it opalescent; but, if abounding in foreign materials, or *hard*, and unfit for washing, it produces more or less opacity or precipitation. X. Liver of sulphur is affected by so many causes, that it may be dispensed with in the examination of waters. Y. Alcohol throws down such salts as it cannot dissolve, especially the sulphates. It dissolves many muriates and nitrates.

I have thus enumerated the tests recommended by BERGMAN, and given an abridged account of his remarks upon them, for the purpose of showing the progress which, under his assistance, was made in analytical chemistry: it is true that of many of these re-agents and of their applications he was not the original inventor; but he was the first who showed the real value and limits of the indications which they afford; an effort of no common sagacity, when we revert to the state of chemistry in his time.

Proceeding with the analysis of mineral waters, BERGMAN next adverts to the gaseous contents, which may be expelled by heating a given portion of the water in a retort, the beak of which is plunged into the mercurio-pneumatic apparatus, and the gas secured in the usual way. It commonly consists of pure air and ærial acid; the latter may be absorbed by lime-water. The presence of hepatic air is easily recognised by its odour. The remaining water is directed to be evaporated to dryness, and the residue weighed and digested in pure alcohol; the residue, insoluble in alcohol, is then to be shaken with eight parts of cold water; and finally, the matters which resist the action of alcohol and cold water are to be boiled in four or five hundred parts of distilled water, and the solution filtered. The ultimate residuum generally contains iron and carbonate of lime, or perhaps of magnesia, previously suspended by

carbonic acid; it may be in a few instances argillaceous or silicious, and perhaps contains manganese, and directions are given at length for its separate analysis, as well as that of the aqueous and alcoholic solutions. It is here that BERGMAN displays an ingenuity and accuracy then new to chemical science, for, in measuring his merits by a true estimate, we must go back to the state of chemistry at his time, and divest ourselves of its modern perfections and refinements; then the peculiar and genuine character of his researches will become prominent.

Having, in the paper of which the above is an outline, described the general principles of the analysis of mineral waters, BERGMAN proceeds, in several following essays, to apply them to individual analyses, and his dissertations on the waters and acidulous spring of Upsal, on sea-water, and on the artificial preparation of hot and cold medicated waters, each exhibit proofs of his skill as an analyst, and accuracy as an experimenter; but, although these and his other detached essays are excellent in their way, we must here pass them by, in order to examine such of his contributions as tended to the general improvement and extension of chemical science; among these, his luminous dissertation on chemical attraction*, already adverted to, is pre-eminent; and the twenty-fourth essay in the second volume of his *Opuscula*, entitled *De Minerarum Docimasia Humida* (on the Art of Assaying in the Humid Way), must be considered as the parent source of that branch of analytical chemistry so successfully followed up, though upon a limited scale, by SCHEELÉ, and in the improvement and extension of which KLAPROTH passed his long and laborious life.

It must be premised that the assay or analysis of minerals had, with the exception of the experiments of MARGRAAF†, hitherto been confined to certain operations effected by the aid of fire, in which, except in

* *De Precipitatis Metallicis.*

† Among those whose names became eminent in the history of chemical science during the first half of the eighteenth century, Margraaf is entitled to particular mention. He was born at Berlin, in 1709, where he died in 1782. He was a pupil of the once celebrated Neumann, a man whose works are now not much thought of, but who did considerable service to the chemistry of his day. Caspar Neumann was born at Züllichau, in Prussia, in 1682; and in 1705 we find him enjoying the patronage of the King of Prussia, by whom he was sent to complete his studies at the university of Halle. In 1711 he became a pupil of Boerhaave, and shortly after visited England, whence he accompanied George I. to Hanover, in 1716. In 1723 he became Professor of Practical Chemistry in the Royal College of Berlin, where he died in 1737. His works consist chiefly in dissertations on various subjects of chemical inquiry, published in the *Transactions of the Royal Society*,

and in the *Miscellanea Berolinensia*. His Lectures were not printed till after his death, and proved a valuable magazine of chemical knowledge. "The author," says Dr. Lewis, who edited his works, "biassed by no theory, and attached to no opinions, has inquired by experiment into the proportions and uses of the most considerable natural and artificial productions, and the preparations of the principal commodities which depend on chemistry, and seems to have candidly and without reserve communicated all he discovered." In 1733, Margraaf pursued chemistry under Juncker, at Halle, and, having returned to Berlin, in 1738, we find several of his contributions in the *Transactions of the Scientific Society*, of that capital. Subsequent to that period his works were collected and published at Paris in 1762. They contain a great body of information, at that time novel and important, but they are chiefly entitled to notice as furnishing specimens of the art of analysis.

common and obvious cases, their nature was rather guessed at than demonstrated. This art had its origin in the sixteenth century; and in 1576 the celebrated work of AGRICOLA brought before the public all that was important in relation to it, describing the instruments and processes with scrupulous and minute accuracy, and illustrating them by a curious collection of cuts. AGRICOLA was succeeded by LAZARUS ERCKERN, whose work on the docimastic art is much eulogized by BOERHAAVE. In the above-named essay BERGMAN points out the fallacies and imperfections to which igneous analysis is liable, and dwells upon the advantage of operating in the humid way, that is, by solvents and precipitants. He then proceeds to separate examinations of various metallic ores, as illustrations of his new method. Many of the conclusions and reasonings contained in this essay are founded upon the details of the preceding one on Metallic Precipitates. "He," says our author, "who first saw the corrosion of a metal by a limpid liquid, who beheld the opaque and ponderous body gradually disappear, and become a part of a transparent and apparently homogeneous fluid, and who saw the same metal re-appear upon the addition of a proper precipitant, must have been infinitely surprised, and struck with admiration of the occult powers of nature. But because we are accustomed to these phenomena, we neglect inquiring into their causes, though of the utmost importance, as forming the entire basis of practical chemistry. Such phenomena are so varied and intricate that volumes would be insufficient for their complete discussion; so that I propose to limit my observations to the separation of metals from acids, and to the particular consideration of *the weights of the precipitates*." Then, after a luminous summary of the general phenomena of the solution of metals, he advances a series of facts relating to their precipitation; he shows that the caustic fixed alkalis occasion precipitates of the *calces*, but loaded with water, by which their weight is much increased: that carbonated alkali precipitates carbonated oxides by double decomposition: that certain acids, which form insoluble compounds with metals, throw them down from their soluble compounds: that certain salts act in the same way by double elective attraction; and that in some cases triple combinations ensue, as when platinum is precipitated by sal ammoniac. He then adverts to the decomposition of one metallic salt by another, even where the acid is the same in both. Thus, sulphate of iron and muriate of tin decompose muriate of gold. The metals also precipitate one another after a certain order, which is the same in all acid solvents, and effected by double elective attraction, "for the metal to be precipitated exists in the solution in a calcined state, but, being reduced by the phlogiston of the precipitant, falls to the bottom; while the precipitant, being calcined, becomes soluble. Although," he says, "many anomalous circumstances occur in this matter, the order is constant and never inverted." The fifth section of this paper explains the use of tests for discriminating the metals, pointing out the colours of metallic precipitates. "Gold and platinum are only in part separated from acids by the alkalis. Nitrate of silver affords a brown precipitate with caustic, and a white with aerated soda and with muriatic acid. Solution of nitrate of mercury gives a red precipitate with carbonated, and a yellowish, or orange, with caustic alkali. The latter is black, if the solution be prepared

without heat. Nitrate of lead is precipitated, white by caustic alkali, an excess of which re-dissolves the precipitate. Nitrate of copper gives a bright-green compound with aërated, and brown with phlogisticated alkali (prussiate of potash). Iron is thrown down green by aërated alkali, and the precipitate, on exsiccation, becomes brownish-yellow. Tin gives a white cloud with all the alkalis; bismuth, white with water and alkalis; nickel, greenish-white with alkalis and prussiate of potash; zinc and antimony white with all alkalis."

Such is a short abstract of the contents of this section, which, although obscured by the language of the old school, and therefore scarcely, perhaps, intelligible to the chemical student of the present day, abounds in useful and perspicuous details: it is followed by the concluding section, containing a table of the relative weights of precipitates, procured in different ways, from a solution of one hundred parts of metals; and, as BERGMAN observes, "this table, upon proper examination, reveals many mysteries." It seems to have been the general opinion at this period, that the relative weights of precipitates were in all cases the same; that is, one hundred parts of lead, for instance, dissolved by nitric acid, and precipitated by caustic, aërated, and phlogisticated alkali, and by sulphuric acid, would furnish an equal weight of precipitate in each individual instance. Our author here shows the fallacy of this opinion, and demonstrates the difference of weights to depend upon the different proportions of the precipitant contained in the precipitate, and upon the occasional retention of a portion of the solvent. The list of precipitates annexed to this paper will disclose, to the attentive observer, principles analogous to those exhibited by the tables of RICHTER, and upon which one of the main pillars of the theory of definite proportionals may be said to rest.

BERGMAN's essay on fixed air, or as he calls it, *aërial acid*, is the last of which I shall make any particular mention. His chief experiments on this subject were probably made about the year 1770. The dissertation I am now quoting was read, in 1774, before the Royal Society of Sciences at Upsal, and is printed in their *Transactions* for 1775. After describing the several methods of obtaining fixed air by the action of acids upon carbonates, by submitting them to a red heat, and by fermentation, he proceeds to define the meaning of the word *acid*, in order to show that fixed air belongs to that class of bodies; that it is soluble in water, that it has a sour taste, reddens turnsole, and unites to and forms crystallizable compounds with alkalis, destroying at the same time their causticity. He detected this acid in the *marmor metallicum* of CRONSTEDT (carbonate of baryta), and observed the rapidity with which baryta-water absorbs carbonic acid from the air, forming an effervescent precipitate. Speaking of the action of carbonic acid upon lime, he gives a masterly sketch of the principal facts relating to the composition and decomposition of the carbonate of lime: he shows the solubility of calcareous spar in water impregnated with fixed air, and its subsequent deposition, often in small crystals; and the same property is also proved to belong to magnesia. BERGMAN then goes on to discuss the elective attractions of fixed air, of which he gives the following table:—

He says it appears to be the weakest acid known, for it is expelled not only by vinegar, but by the phlogisticated acids of nitre and of vitriol (nitrous and sulphurous acids); yet he observes that acetate of lead as decomposed by carbonic acid, which appears an anomaly, and suggests a question which he leaves undecided till experiment shall have enabled him to explain it. The acid properties of fixed air are next dwelt upon, and the probability of its acidity resulting from foreign matter negatived; for when "rightly depurated, though extricated by the most different means from the most different materials, whether by fire or by solution, it is nevertheless always the same, and always acid. I conclude, therefore, with all the certainty attainable in physics, that acidity is a property essential to that elastic fluid." From the imperfection of apparatus, BERGMAN erred a good deal in calculating the specific gravity of fixed air; he, however, proved it heavier than atmospheric air, and thence accounts for its lodging in low situations, as in pits and grotts: it is also shown to extinguish flame.

AERIAL ACID.

Pure terra ponderosa.
 — lime.
 — fixed vegetable alkali.
 — fixed mineral alkali.
 — magnesia.
 — volatile alkali.
 — Zinc.
 — Manganese
 — Iron.

The essays which I have now quoted, and which may be taken as a fair sample of his method of investigation, exhibit BERGMAN in the light of a true philosopher, employing hypothesis as the precursor, and not the substitute of experiment; countenancing no theory but such as admits of rigid demonstration; advancing no favourite doctrines nor hasty speculations; but always the candid narrator of facts. As the repeater of the experiments of others, he measures and weighs their conclusions, and assigns them their proper place in the history of science. When in the character of an original inquirer, he kindles the torch of experiment, and never advances beyond the boundary of its light. He seems profoundly to have admired Newton, and to have endeavoured to transfuse his methods of investigation into chemistry. "That illustrious personage," he says, "having solicitously accumulated facts, examined them with accuracy, and compared them with acuteness; from effects he advances to causes, and thence deduces the laws of the creation. His progress, though slow, is certain; and his method, though tedious, is continually unveiling the mysteries of nature. An edifice thus constructed acquires firmness by elevation, for its foundations are solid and permanent."

There is more method in BERGMAN than in any antecedent chemical writer; his researches appear always to have been made with an object in view; and there is an unity of design in his philosophical papers, which pleasingly distinguishes them from the undigested chaos of experiments and observations which we are obliged to wade through in many preceding authors.

BERGMAN had many celebrated successors in analytical chemistry, as applied to mineral substances; among these, KLAPROTH and VAUQUELIN have especially contributed to the progress of this branch of the science. MARTIN HENRY KLAPROTH, was born at Wernigerode, in Prussia, on the 1st of December, 1743; and died at Berlin on the 1st of January, 1817.

He was an excellent man, and a diligent and accurate analyst: he was a pupil of ROSE of Berlin, who died in 1771. He published a variety of important papers in periodical works; and in 1795 collected them, under the title of *Beiträge zur Chemischer Kenntniss der Mineralkörper*, (contributions towards the chemical knowledge of mineral substances.) Of this work, consisting of six volumes, the last was published in 1815; it contains not less than two hundred and seven essays*.

VAUQUELIN, who died, at an advanced age in Paris, in 1829, was originally a peasant boy of Normandy. He was employed in Fourcroy's laboratory, where he not only acquired great dexterity in the ordinary duties of his situation, but became an expert and original analyst: he afterwards rose to high eminence in his profession, and his numerous and important contributions and discoveries are lasting monuments of his skill and industry.

Among the mineral analysts and improvers of analytical chemistry in this country, Mr. CHENEVIX deserves honourable mention. The following brief account of his contributions, and of the curious and mysterious controversy respecting Palladium, in which he was at one time involved, I copy from Dr. THOMSON'S *History of Chemistry*, vol. ii., p. 215.

"Mr. Chenevix deserves also to be mentioned as an improver of analytical chemistry. He was an Irish gentleman, who happened to be in Paris during the reign of terror, and was thrown into prison, and put into the same apartment with several French chemists, whose whole conversation turned upon chemical subjects. He caught the infection, and, after getting out of prison, began to study the subject with much energy and success, and soon distinguished himself as an analytical chemist. His analysis of corundum and sapphire, and his observations on the affinity between magnesia and silica, are valuable, and led to considerable improvements in the method of analysis. His analyses of the arseniates of copper, though he demonstrated that several different species exist, are not so much to be depended on; because his method of separating and estimating the quantity of arsenic acid is not good. This difficult branch of analysis was not fully understood till afterwards. Chenevix was for several years a most laborious and meritorious chemical experimenter. It is much to be regretted that he should have been induced, in consequence of the mistake into which he fell respecting palladium, to abandon chemistry altogether. Palladium was originally made known to the public by an anonymous handbill which was circulated in London, announcing that *palladium*, or new silver, was on sale at Mrs. Forster's, and describing its properties. Chenevix, in consequence of the unusual way in which the discovery was announced, naturally considered it as an imposition on the public. He went to Mrs. Forster's, and purchased the whole palladium in her possession, and set about examining it, prepossessed with the idea that it was an alloy of some two known metals. After a laborious

* Professor Frederick Stromeyer of Göttingen, who died in 1835, was a chemist of most distinguished analytical attainments, and deserves to be especially mentioned as one of the successful followers of the methods chalked out by Klaproth. He was Inspector-general of

the Apothecaries for the Kingdom of Hanover; and it was in discharging the duties of that office that he was led to notice certain peculiarities in the oxide of zinc, prepared for pharmaceutical uses: his further inquiries on this subject terminated in the discovery of cadmium.

set of experiments, he considered that he had ascertained it to be a compound of platinum and mercury, or an amalgam of platinum made in a peculiar way, which he describes. This paper was read at a meeting of the Royal Society by Dr. Wollaston, who was secretary, and afterwards published in their *Transactions*. Soon after this publication, another handbill was circulated, offering a considerable price for every grain of palladium made by Mr. Chenevix's process, or by any other process whatever. No person appearing to claim the money thus offered, Dr. Wollaston, about a year after, in a paper read to the Royal Society, acknowledged himself to have been the discoverer of palladium, and related the process by which he had obtained it from the solution of crude platina in aqua regia. There could be no doubt after this, that palladium was a peculiar metal, and that Chenevix, in his experiments, had fallen into some mistake, probably by inadvertently employing a solution of palladium, instead of a solution of his amalgam of platinum; and thus giving the properties of the one solution to the other. It is very much to be regretted that Dr. Wollaston allowed Mr. Chenevix's paper to be printed, without informing him, in the first place, of the true history of palladium; and I think that if he had been aware of the bad consequences that were to follow, and that it would ultimately occasion the loss of Mr. Chenevix to the science, he would have acted in a different manner. I have more than once conversed with Dr. Wollaston on the subject, and he assured me that he did everything that he could do, short of betraying his secret, to prevent Mr. Chenevix from publishing his paper; that he had called upon, and assured him, that he himself had attempted his process without being able to succeed, and that he was satisfied that he had fallen into some mistake. As Mr. Chenevix still persisted in his conviction of the accuracy of his own experiments after repeated warnings, perhaps it is not very surprising that Dr. Wollaston allowed him to publish his paper; though, had he been aware of the consequences to their full extent, I am persuaded that he would not have done so. It comes to be a question whether, had Dr. Wollaston informed him of the whole secret, Mr. Chenevix would have been convinced."

The Honourable EDWARD HOWARD also deserves a place among those eminent for their contributions to analytical chemistry. He was the first who accurately examined meteoric stones, and showed their identity from various places. (*Phil. Trans.*, 1802.)

§ XII.

BERGMAN was followed by two great and contemporary luminaries of chemical science, CAVENDISH* and SCHEELÉ, and though each attained distinction, they reached it by very different roads; showing the little influence of external circumstances upon the growth of inherent genius. The former was a leading person in the scientific circles of London; of noble family, and princely affluence. The latter, of humble origin and with limited means, made up for the deficiencies of place and fortune by zeal and economy, and, in the retirement of a Swedish village, raised a reputation that soon extended itself over Europe. In private life,

* Born in London, 1731; died at Clapham, 1810.

CAVENDISH was unambitious, unassuming, bashful, and reserved; he was peevishly impatient of the inconveniences of eminence; he detested flattery, and was uneasy under merited praise: he therefore shunned general society, and was only familiar in a very limited circle of friends. He was in the habit of dining every Thursday at the Royal Society Club, and there he always bore his faculties meekly; his conversation was varied and instructive; upon all subjects of science he was at once luminous and profound, and in discussion wonderfully acute.

Mr. CAVENDISH made two capital discoveries; one of which, that of the composition of nitric acid, has already been adverted to, and arose out of his researches on hydrogen, and on the products of its combustion, which terminated in ascertaining the composition of water. His first communication to the Royal Society relates to the analysis of the waters of Rathbone Place, and contains nothing worthy of particular notice. In 1776, he presented the same learned body with a dissertation on Inflammable, Fixed, and Nitrous Air, printed in the *Philosophical Transactions* for the same year, and full of important and original matter. Though his observations on fixed and on nitrous air were highly valuable, he had here been anticipated in some respects, and contemporary chemists were on most points his successful rivals; but his investigations relating to the properties of hydrogen were entirely his own; for, although it was known to others that that gas was generated by the action of certain acids on certain metals, though MAYOW had collected it, and HALES proved its combustibility, it may safely be asserted, that the phenomena of its production had entirely escaped attention, and that its principal properties were previously unknown. CAVENDISH shows that different metals afford different quantities of hydrogen; thus zinc yielded more than iron, and iron more than tin; and further, that the state of dilution and quantity of the acid, provided there was enough to dissolve the metal, did not affect either the quantity or properties of the air. In examining its properties, our author observed that it extinguished flame, destroyed animal life, and burned when pure with a pale blue flame: he determined its specific gravity, and found it was the lightest of all ponderable matter; hence its subsequent suggestion by Dr. BLACK and Mr. CAVALLLO as a substitute for rarefied air in the balloon: the former indeed failed in its application, and the latter only succeeded in the pretty experiment of elevating soap-bubbles by inflating them with hydrogen: he tried bladders, but the thinnest were too heavy, and tissue paper was permeable to the gas; it is singular he did not think of gold-beaters' skin, which, for similar purposes, had been recommended two centuries before by SCALIGER the grammarian*.

The first ascent in a balloon filled with hydrogen was made on the 1st of December, 1783, by Messrs. CHARLES and ROBERT, at Paris. In an hour and three-quarters, they alighted on the meadow of Nesle, twenty-five miles from the metropolis, and finding that the silk globe still retained great buoyant power, M. CHARLES ventured alone upon a second ascent. The sun had set, and the shades of evening were gradually condensing into the darkness of night; but his courage was rewarded by a most novel and sublime spectacle. He shot upwards with such celerity as to

* Supplement to *Encyclopædia Britannica*, Art. *Aëronautics*.

have attained the height of two miles in about ten minutes. The sun rose again to him in full orb, and from his lofty station he contemplated the fading luminary, and watched its parting beams till it once more sunk below the horizon. The vapours rising from the earth collected into clouds, and veiled it from his sight, while the pale rays of the moon scattered gleams of various hues over the fantastic and changing forms. The region in which the *aéronaut* now hovered was extremely cold; the balloon appeared fully distended, and upon opening the valve, the gas rushed out like a misty vapour into the external air. Prudence forbade this bold voyager to remain longer in such a situation; slowly therefore descending, he alighted in safety near the forest of Tour du Lay, having travelled about nine miles in thirty-five minutes. The barometer at the greatest elevation fell to 20.05 inches, and the thermometer sunk to 21° Fahrenheit; he therefore appears to have ascended to about 9,700 feet above the level of the sea.

The balloon has unfortunately proved but an abortive instrument in the hands of science. Messrs. BIOT and GAY-LUSSAC embarked from Paris on the 23rd of August, 1804, upon an *aërial* excursion devoted entirely to scientific inquiry. At the height of 13,000 feet, no peculiarity appeared to attach to electric or magnetic phenomena. On the 5th of the following September, GAY-LUSSAC undertook a second voyage alone, and attained the enormous height of 23,040 feet above the sea. Here he experienced excessive cold, his breathing was oppressed, and the pulse quickened; he, however, did not suffer the peril of his situation, or the peculiarities of his sensations, to distract his attention, and made several magnetic, electric, and hygrometric observations, without either novel or interesting results. Having alighted in safety in the neighbourhood of Rouen, he returned to Paris, and in the presence of M. THENARD analyzed the air brought from the upper regions, which proved analogous in composition to that at the surface of the earth.

To return to CAVENDISH: having determined the specific gravity, and other abstract properties of hydrogen gas, he proceeded to examine the results of its combustion, and found that, when mixed in certain proportions with atmospheric air, it exploded on the contact of flame, and deposited moisture in the vessel used for the experiment, a circumstance first noticed by MACQUER in 1766, and distinctly referred by WATT to the production of water in 1783. The experimental proofs, however, were still insufficient, and were supplied by CAVENDISH, in a paper given to the Royal Society in 1784. He found that a stream of pure hydrogen; burned either in air or oxygen, produced a vapour condensible into pure water. The same product resulted from the rapid combustion of a mixture of inflammable and dephlogisticated airs (hydrogen and oxygen gases). These experiments were subsequently verified by analytical researches: water was decomposed by LAVOISIER, by passing steam through a red-hot tube containing iron, which absorbs its oxygen, and pure hydrogen is liberated in the gaseous form. The decomposing energies of electricity have also been applied to this fluid, and it is found uniformly to be resolved into one volume of oxygen and two of hydrogen, which disappear on passing an electric spark through the mixture, and are converted into their weight of pure water.

The discovery of the composition of water, due to the joint labours of CAVENDISH and WATT, was a great step in chemical science, for it developed the hidden cause of many important phenomena of art and nature: no wonder, then, that the attention of the theorists was especially fixed upon it, some applying it to the explication of all difficulties; others rejecting even legitimate conclusions, and unwilling to strike this favourite element from the list of simple bodies.

CAVENDISH was an enemy to the new Nomenclature of chemistry, and was fond of foretelling its downfall; he disliked all innovations that were not rendered absolutely necessary by the progress of experiment, and would never adopt new opinions till fully and leisurely convinced of the fallacy of old ones.

While PRIESTLEY and CAVENDISH were contributing to the chemical eminence of Britain, SCHEELÉ* was diligently employed in the same pursuit under the patronage and guidance of BERGMAN, of whom it has been emphatically said, "that his greatest discovery was the discovery of SCHEELÉ," for he was the first to remark his promising genius and rising merit.

SCHEELÉ's publication, entitled *Chemical Observations and Experiments on Air and Fire*, is prefaced by an Introduction from the pen of his patron BERGMAN, setting forth the advantages of experimental science, and the benefits likely to result from the application of chemistry to the treatment and cure of diseases. Finding air necessary for the production of fire, SCHEELÉ first turned his attention to its analysis: he found that solution of liver of sulphur, and certain other sulphureous compounds, occasioned a diminution in the bulk of air to which they were exposed, equal to about one part in five; the flame of hydrogen, and that of sulphur, caused a similar decrease of bulk in air standing over water, and lime-water not being rendered in either case turbid by the residuum, no fixed air was formed. He then obtains empyreal air, (oxygen,) by the decomposition of nitric acid, and other processes; describes the method of transferring, collecting, and examining the gases; and endeavours to prove that heat is a compound of empyreal air and phlogiston; he also shows, by a direct experiment, that the absorption occasioned in atmospheric air by liver of sulphur is referable to the abstraction of its empyreal portion; that it totally absorbs empyreal air; and that upon adding to the residuary portion of atmospheric air, a quantity of empyreal air equal to that absorbed by the sulphureous liquor, an air is again compounded, similar in all respects to that of the atmosphere. The identity of these investigations

* Scheele is among the fortunate few, who, starting from an obscure original, have attained the zenith of scientific eminence. He was born in 1742, at Stralsund, where his father was a tradesman. His youthful days were passed in the house of an apothecary at Gottenburgh, where, by singular perseverance, and that kind of industry which is prompted by strong natural inclination, he acquired a valuable stock of chemical information. In 1773, having removed to Upsal, accident brought him acquainted with Berg-

man, who became his friend and patron, and to whose honour be it told, that, when Scheele's reputation afterwards rose to such a height as threatened to eclipse his own, instead of listening to the voice of jealousy, which, on such occasions, is too common a frailty, he became more zealous in behalf of his rival, and more indefatigable in the service of his friend. Scheele afterwards removed to Köping, in the neighbourhood of Stockholm, where he died in 1786.

with those of PRIESTLEY will not fail of being observed; but it must be recollected that they were entirely independent, and that although PRIESTLEY was in the field a little before him, SCHEELE was unacquainted with his proceedings.

The details concerning the nature of air, are followed by an inquiry into the properties of Heat and Light, which, though somewhat tainted by false theory, bears the stamp of an able and original mind. Adverting to the reflection of the rays from a common fire, by a concave metallic mirror, he remarks, that they passed in straight lines, without suffering any derangement from currents or undulations in the atmosphere which they traverse; that glass intercepts the heat, but not the light; that a mirror of glass reflects the light, but absorbs the heat, whereas metal reflects both: the metal, therefore, if clean, does not become heated; but, if blackened over a smoking candle, it then absorbs heat, and becomes very warm. He notices the distinction between heated air and heat emanating in straight lines: "represent to yourself a little hillock of burning coals; in this case, the heat darting from this hillock all around is that which may be reflected by a metallic polished plate; that, on the contrary, which rises upwards, and may be driven by winds to and fro, unites with air. I call the first kind, by way of distinction, *radiant heat*." Discussing the phenomena of solar and terrestrial radiation, he considers their apparent differences to result, not from any absolute difference in the nature of the emanating particles, but in their quantity. "There is no doubt," he says, "about the light of the sun and that of a burning candle being the same thing; for this affects the eye in the same manner as the sun, and represents the same colours through the prism, but being weaker, it is no wonder that its beams, collected in a burning-glass, will not burn: nor is there any doubt about light being a body in the same manner as heat, but I cannot persuade myself that light and heat are the same thing, since experiment proves the contrary." Finding that light blackened nitrate of silver, though heat alone had no effect upon it, he considers light as containing an inflammable principle, and shows that *luna cornea*, after long exposure to the sun's rays, is no longer perfectly soluble in ammonia, but leaves a portion of reduced silver; he also shows, that when put into water, it forms muriatic acid in the light, but not in the dark; and that the violet rays produce these effects more rapidly and powerfully than the other coloured rays, and even than white light.

Among these experiments on air and fire some curious facts are detailed, respecting the spontaneously inflammable compound discovered early in the last century by HOMBERG, and called *Pyrophorus*; it is shown that potash is necessary to its formation, and that alum crystallized by ammonia is unfit for its production. The evolution of hydrogen, during the action of iron upon sulphur, and of nitrogen in the detonation of fulminating gold, are also among the facts contained in this essay; as well as a variety of curious circumstances relating to the effect of vegetation and respiration upon air; and it closes with an account of the properties of Sulphureted Hydrogen.

Exclusive of the experimental details, there is little to praise in the *Treatise on Air and Fire*, for the theories which it contains are often

strained and illicit, and do not easily admit of being rendered intelligible by the translation of the phlogistic language into that of the modern school: nor are SCHEELE's detached essays altogether free from similar blemishes; but then they are so rich in facts, that we the more easily overlook theoretical failings. His dissertation on Manganese, for instance, with a description of the principal salts of that metal, contains the important discovery of Dephlogisticated Muriatic Acid, or, as it is now termed, Chlorine; and his views respecting it, and the nature of the muriatic acid, are remarkably correct, and perfectly intelligible in present theory, if we substitute hydrogen for phlogiston; it will then be found that muriatic acid is regenerated by the addition of hydrogen to chlorine, and that hydrogen is evolved by the abstraction of chlorine from muriatic acid.

BERTHOLLET's hypothesis of the nature of chlorine for a time superseded the theory of SCHEELE, and under the name of Oxymuriatic Acid, it was regarded as a compound of oxygen and muriatic acid; but, in 1811, Sir H. Davy, in an important dissertation on the subject, published in the *Philosophical Transactions*, demonstrated the errors of the French school, revived the doctrine of SCHEELE, and established it by a body of evidence now generally received. Berthollet, however, has the distinguished merit of first suggesting the application of chlorine to bleaching upon the large scale.

In his essays on Fluor Spar, and its acid, SCHEELE has committed several errors, among which the most glaring is the conclusion which he draws respecting the formation of siliceous earth. When powdered fluor spar is distilled with sulphuric acid in a glass retort, the silica of the glass is dissolved by the acid of the fluor, carried over with it in the gaseous state, and in part deposited in the receiver containing water; SCHEELE inferred that siliceous earth was here formed by the union of fluoric acid and water; and, persisting in his error, he endeavours to show that the same formation ensues in metallic vessels, and therefore independent of glass; but he takes no due precautions against the presence of silica in the fluor spar which he used. Yet there is much to praise in the methods of analysis employed in investigating the nature of this singular body; it is a subject full of difficulties, and can scarcely be called complete even at the present day, though it has engaged the attention of the most acute analysts. The acids of arsenic and of molybdenum were first examined by SCHEELE, and he first showed the difference between Molybdenum and Plumbago, and pointed out the existence of carbon and iron in the latter.

In 1778, SCHEELE made known the preparation of Arsenite of Copper, and recommended it as an useful and permanent colour in oil and water painting; and, in 1779, he took up the important subject of the decomposition of neutral salts by unslaked lime and iron. He found upon the iron hoops of a tub of salted turnips, which had been placed in a damp cellar, a quantity of salt resembling mineral alkali, and was struck with the circumstance, "knowing that the attraction of acid of salt is weaker for iron than for mineral alkali." He dipped plates of several other metals into solutions of common and Glauber's salt, but found that iron only was effectual in their decomposition, and that the action was more rapid in a damp cellar than elsewhere; he also found that quicklime

decomposed those salts in the same situation; and that the decomposition was partly dependent upon the presence of carbonic acid in the atmosphere of the vault.

In the essays on Milk and Sugar-of-milk, there are many curious circumstances respecting the action of re-agents upon that liquid, and these papers deserve particular notice, as among the earliest specimens of the analysis of animal fluids. SCHEELE observes that, from his experiments, it appears "that the acid of milk is an acid of a peculiar kind, and though it expels the vinegar from acetated vegetable alkali, yet it seems destined, if I may so speak, to be vinegar." He attributes its difference to the want of some ferment, and shows that the addition of a little brandy to milk, causes it, when fermented, to afford good vinegar. The method of obtaining the Citric and some other vegetable acids, by decomposing their compounds with lime by sulphuric acid, is also among SCHEELE's discoveries; and his essays on Tungsten, on the preparation of Calomel in the humid way, on Urinary Calculi, on Ether, and on Benzoic acid, each contain important facts, and display new modes of inquiry: they deserve the perusal of those who may be engaged in investigations relating to the several subjects of which they treat.

The last essay to which I shall advert in this sketch of SCHEELE's discoveries, was published in 1782, and is entitled *Experiments on the Colouring Matter of Prussian Blue*. This very singular substance was accidentally discovered early in the last century, by DIESBACH, a colour-maker at Berlin: the preparation was, however, kept secret till published by WOODWARD, in 1724. In 1752, MACQUER's dissertation upon it presented a connected view of its chemical history, which, however, was imperfect and unsatisfactory. SCHEELE directed his attention to the discovery of the principle upon which its colour depended. He shows, that the salt produced, by digesting Prussian blue in caustic potash, is a triple compound of the colouring principle, iron and potash; iron being, as he supposes, the medium by which the colouring matter is attached to the alkali: this salt he decomposed by distilling its aqueous solution with a small quantity of concentrated vitriolic acid, and the liquor which passed into the receiver carried with it a great portion of the colouring principle, which has since been termed *Prussic Acid*. SCHEELE then goes on to show that the action of this acid, in its pure state, upon metallic solutions, is very different from that which it exhibits when combined with alkalis. United with lime, he found that it afforded precipitates in the greater number of metallic solutions. Our author enters into much interesting speculation and experiment, relating to the nature of this colouring principle; and considering the difficulty of the subject, treats it with perspicuity and success. This dissertation on Prussian blue was nearly his last contribution to the science which he had so much embellished and improved, for he died in 1786, at the age of forty-four.

It requires no deep inquiry, or minute investigation, to detect, in the researches of PRIESTLEY, SCHEELE, and CAVENDISH, the materials of which their contemporary, LAVOISIER, aided by several celebrated chemists of the French school, constructed his new theory; and a retrospect of the works of MAYOW and HOOKE will show that the Antiphlogistic System almost necessarily arose out of a combination of their views with the more

modern discoveries. In maintaining, however, that the materials employed in raising this celebrated system were of foreign, and chiefly of British origin, we must not be understood as detracting from the indisputable merit of those to whose persevering diligence chemistry owes so much of its present importance; by whom the scattered and unconnected facts of the science were brought together and arranged; and who cleared its paths of the numerous obstructions with which they were previously beset.

§ XIII.

THE numerous and important contributions with which the eminent but unfortunate LAVOISIER* enriched the chemistry of his time are to be found in the *Memoirs of the Royal Academy of Sciences of Paris*; but as he has chiefly been celebrated as a theorist, I shall here confine myself to such of his inquiries as bear upon that memorable reform in the science, by which a new nomenclature was introduced, and which ended in the banishment of phlogiston. In this reform LAVOISIER took the lead, and though his original investigations connected with it are few and comparatively unimportant, he availed himself with so much skill and success of the labours of others, as, by placing them in new points of view, and exhibiting their unexpected applications, to render them almost his own. LAVOISIER's character has, in some measure, suffered by the misguided zeal of his admiring commentators, who, not satisfied with allowing him due merit for the logical precision and sagacity of induction which he brought into chemistry, have represented him as having the experimental activity of PRIESTLEY, and the laborious diligence of SCHEELE. But LAVOISIER, though a great architect in the science, laboured little in the quarry; his materials were chiefly shaped to his hand, and his skill was displayed in their arrangement and combination.

A connected view of his principal reasonings and most prominent researches will be found in his *Elemens de Chimie*, published at Paris, in 1789. This work, in every way important, is divided into three principal sections: the first treats of the formation and decomposition of aëriiform fluids, of the combustion of simple bodies, and the formation of acids: the second, of the combination of acids with salifiable bases, and of the formation of neutral salts: and the third, of the instruments and operations of chemistry.

The first section opens with a discussion concerning the Nature and Operations of Heat, which he defines as a real and material substance, or a very subtile fluid, separating the particles of bodies from each other, by insinuating itself among them. This exquisitely attenuated substance he calls *Caloric*, and though he allows that light, in many instances, produces phenomena analogous to those of heat, though they have certain qualities in common, their identity not having been demonstrated, they are to be considered as distinct; he then dwells upon the requisite caution in investigating the properties of caloric, since they are known

* Born in 1743 at Paris, where he fell a victim to the Revolution, on the 8th of May, 1794.

only by fleeting and difficultly ascertainable effects: "It is in those things," he says, "which we neither see nor feel, that it is especially necessary to guard against the extravagances of the imagination, which always inclining to overstep the bounds of truth, is difficultly restrained by the narrow limits of facts." The influence of heat upon the states of bodies is then illustrated, and their relative capacities for heat alluded to. He says that solidity, liquidity, and aëriform elasticity, are only three different states of existence of the same matter, or three particular modifications which almost all substances are susceptible of assuming successively, and which solely depend upon the degree of temperature to which they are exposed, or, in other words, "upon the quantity of caloric with which they are penetrated." In consequence of this influence of caloric, the possible existence of certain metallic substances in our atmosphere is inferred; "such a substance, for instance, a little more volatile than mercury, might exist there." LAVOISIER then proceeds to the analysis of atmospheric air, which he effects by exposing fifty cubical inches of it to heated mercury; it undergoes a decrease equal to one-sixth of its original bulk, and becomes unfit for respiration and combustion; at the same time, the quicksilver is partly converted into a reddish matter, 45 grains of which heated red-hot in a proper retort, afforded 41.5 of running mercury, and 7 or 8 cubical inches of gas, eminently supporting combustion, and being the dephlogisticated air discovered by PRIESTLEY. The mixture of the 42 cubical inches of the mephitic air of the retort, with the 8 cubical inches of dephlogisticated air, separated from the mercury, re-produce 50 cubic inches of atmospheric air.

LAVOISIER considered all aëriform fluids as compounds of a ponderable basis, with caloric and light: in the above experiment, the ponderable part of the dephlogisticated air unites to the quicksilver, but the union is effected so slowly, that the phenomena of combustion are not perceived; if, however, red-hot iron wire be introduced into the air evolved from the red compound of quicksilver, it acts readily upon it, and its decomposition is attended by the copious evolution of heat and light, while the iron undergoes an increase in weight equivalent to that of the air absorbed.

In discussing the principles of nomenclature, most applicable to the different aëriform fluids, LAVOISIER retains, after the example of MACQUER, the word *gas*, used first by VAN HELMONT, as a generic term for all that differ from atmospheric air: he shows that one of the most general properties of vital or dephlogisticated air, is, to form *acids*, and hence he gives it the name of *oxygen gas*; the other element of the atmosphere is called *azotic gas*, from its fatal effects upon animal life, a term, "commendable," says LAVOISIER, "because it only expresses a matter of fact."

The combustion of sulphur, phosphorus, and carbon, is next shown to be attended with the same phenomena as that of iron, namely, the extrication of heat and light, and the union of the ponderable part of the oxygen with the combustible; and the principles of nomenclature applicable to these different compounds are developed. Where oxygen does *not* form an acid, its compounds are termed *oxides*; and where more than one oxide, or acid, is formed, the termination of the base

indicates its nature: thus there are four compounds of nitrogen with oxygen, two oxides, and two acids; the former are respectively termed *nitrous* and *nitric oxides*; and the latter, *nitrous* and *nitric acids*; the *minimum* and *maximum* of oxygen being in each case designated by the termination *ous* and *ic*. The term *hydrogen* is applied to inflammable air, shown by CAVENDISH to be the basis of *water*; and fixed air is called *carbonic acid*, since it is identical with the result of the combustion of charcoal, or carbon, in oxygen. In connexion with the latter subject, LAVOISIER made the important discovery of the production of carbonic acid by the combustion of the diamond. The destruction of this gem by fire was demonstrated by the Florentine Academicians as early as 1690; they exposed a diamond to the focus of a burning lens, and found that it was entirely evaporated; and Francis the First, of Germany, witnessed the same phenomenon in the heat of a furnace. LAVOISIER proved that the diamond underwent no change when air was excluded; and that, when ignited in oxygen gas, it produced carbonic acid: whence the inevitable conclusion that the diamond and charcoal are identical in their nature; and that the vast difference in their appearance and mechanical qualities is the result of aggregation; that the one is crystallized; the other in a less indurated form. Unprecedented as such an idea may seem, it is not only warranted by the experiments of LAVOISIER and others, but also in some degree supported by analogy. Thus, when argillaceous earth, which is a white pulverulent substance, is aggregated by mechanical attraction into a crystalline form, it constitutes the sapphire, one of the hardest and least destructible of the gems. In one state, the earth is soft, and readily soluble in acids; in the other, its insolubility equals its induration: but there is one anomaly, relating to the conducting power of the diamond and charcoal in regard to electricity; the former ranks among the non-conductors, the latter is a good conductor; and hitherto mechanical texture has not been clearly shown, in any strictly analogous cases, to interfere with the power of conducting electricity.

Among those who have further explored the phenomena of the combustion of the diamond, and who have verified and extended the original views of LAVOISIER, we find the names of some of the most eminent European Philosophers. Few subjects in Chemistry have been so carefully pursued, and the united results of different experimentalists have rarely tallied with the precision which these researches present*.

* That the quantity of carbonic acid, afforded by a given weight of diamond, is the same as that yielded by a similar quantity of charcoal, is the great proof of the identity of those apparently dissimilar substances; this was demonstrated in the year 1796, by the refined and elegant experiments of the late Mr. Tennant.

Mr. Smithson Tennant was a profound philosopher, and a matchless companion: "his learning was without pedantry; his wit without sarcasm;—he was deep, but always clear; gentle, but never dull." To those who knew him not, it is scarcely possible to offer an adequate representation of his singularly pleasing and

enlightened character; by those who enjoyed his acquaintance, and partook of his social hours, his extent of knowledge, his happy and unrivalled talent for conversation, his harmless but brilliant flashes of merriment, and all his amiable peculiarities, can never be forgotten. Mr. Tennant was born in Yorkshire in 1761, and died at Boulogne in 1815. He was the discoverer of the metals Iridium and Osmium, and the author of several important contributions to chemical science.

See Biographical Account of Smithson Tennant, Esq., in THOMSON'S *Annals of Philosophy*, vol. vi.

LAVOISIER was the first who examined with requisite accuracy the products of the distillation of vegetable and animal substances, and who drew a proper line of distinction between the *educts* and *products* thus afforded; he also inquired, with more success than any of his predecessors, into the phenomena of *fermentation*, and by examining the contents of certain vegetable juices previous to and after that process, he drew some very curious conclusions respecting the changes that take place.

In his observations upon *salifiable bases*, and the formation of *neutral salts*, LAVOISIER has described the phenomena of the solution of metals in the various acids: he adverts to the oxidizement of the metals previous to their solution, and to the consequent liberation of hydrogen; and has the following acute surmise respecting the nature of the alkaline earths, which then were considered as elementary bodies:—"From these phenomena it appears that oxygen is the bond of union between metals and acids, and from this we are led to suppose that oxygen is contained in all substances which have a strong affinity with acids; hence it is very probable that the four eminently salifiable earths contain oxygen, and that their capability of uniting with acids is produced by the intermediation of that element. What I have formerly noticed relative to these earths, namely, that they may very possibly be metallic oxides, with which oxygen has a stronger affinity than with carbon, and consequently are not reducible by any known means, is considerably strengthened by the above considerations." Sir H. DAVY, in showing the combustibility of the metals of the alkalis in carbonic acid, has verified this anticipation.

In the second part of the *Elements*, LAVOISIER treats of the formation of Neutral Salts, and throws out new and important views relating to the constitution of chemical compounds. Speaking of the influence of Light as a chemical agent, he adverts to its singular action upon the vegetable kingdom, and supposes that it combines with certain parts of vegetables, and that the green of their leaves, and the various colours of their flowers, are chiefly owing to this combination. "This much," he says, "is certain, that plants which grow in darkness are perfectly white, languid, and unhealthy, and that to make them acquire vigour, and recover their natural colours, the direct influence of light is absolutely necessary. Somewhat similar takes place even in animals. Mankind degenerate to a certain degree when employed in sedentary manufactures, or living in crowded houses, or in the narrow lanes of large cities; whereas they improve in their nature and constitution in most of the country labours which are carried on in the open air."

LAVOISIER incorrectly refers the influence of light to its direct combination; but it rather appears to modify, or exalt, the mutual agencies of bodies: of this we have some remarkable instances; as in the action of chlorine upon hydrogen, and upon carbonic oxide; and of chlorine, and several of the chlorides, upon water; from which it occasions the evolution of oxygen, and the production of muriatic acid; this change gave rise to the idea of the existence of oxygen and muriatic acid as the components of chlorine; the agency of water and the nature of muriatic acid not having been taken into the account.

In his observations on the combinations of oxygen, the conditions requisite to the oxidizement of bodies are mentioned; such as the dimi-

nution of aggregation by heat, which causes many substances to attract the oxygen of the atmosphere; their ignition with nitre, or with chlorate of potassa; and their solution in certain acids, especially the nitric. The combinations of the different combustible substances are next reviewed, and those of the acids and of some other compound bodies.

The third part of the *Elements* is occupied with the description of a variety of chemical operations, which were exceedingly improved and extended by LAVOISIER. He shines as the inventor of costly and complicated apparatus, the greater part of which might, however, have been superseded by simpler and cheaper utensils.

This sketch of the contents of LAVOISIER's *Elements of Chemistry* will sufficiently show the extent and perspicuity of his views as a theorist; and though the arrangement is open to objection, it was calculated for the use of the student, and fitted to display the strongest parts of the anti-phlogistic system in the most favourable light: it was, indeed, impossible that any one of unbiassed judgment could seriously retain the phlogistic doctrines after the perusal of this masterly refutation. If we look for the abstract facts upon which this refutation rests, we shall search in vain, either in the works of LAVOISIER, or in those of his contemporaries: they were furnished from other quarters, and will, I think, chiefly be found in the writings of MAYOW and HOOKE, and in those of PRIESTLEY and SCHEELÉ. The prominent features of the French theory are its explanation of the phenomena of combustion and of acidification, the presence of oxygen being deemed essential in both cases. That air is the food of fire was known in the remotest ages; that it causes the increase of weight sustained by metals during their fusion and calcination, was shown by REY early in the seventeenth century; that a part only of the atmosphere, is concerned in the support of flame, was explained by HOOKE in 1667; and that the vital or igneous spirit, as he terms it, of the atmosphere, is concerned in the formation of acids, was asserted by MAYOW in 1674. Here, without advancing into the eighteenth century, we have, in explicit detail, all the facts and arguments requisite for the construction of the French theory; but if to these we add the discovery of Oxygen by PRIESTLEY, and of the composition of water by CAVENDISH and WATT, what then becomes of its claim to originality?

It must be regretted that those who have censured LAVOISIER with occasional uncandid and unacknowledged appropriation of the thoughts of others, have some grounds for the accusation. In bringing forward his theory of combustion, why did he not refer to the opinions of REY and MAYOW? why refuse praise and acknowledgment to BLACK, and SCHEELÉ, and CAVENDISH; or why appropriate the discovery of oxygen, in the face of the prior, indisputable, and known claims, of his friend and contemporary, PRIESTLEY? These are questions we cannot now answer; but those who have grounded indiscriminate and severe censure upon such accusations, have neither been animated by the unprejudiced spirit of true philosophy, nor guided by the unbiassed love of truth. It must be remembered that LAVOISIER was never fairly confronted by these rivals and antagonists; that unintentional inadvertency often accompanies scientific ardour; that, in the eagerness of pursuit, he may have neglected that which, in a calmer hour, he would have seen, regretted, and acknowledged;

and that, in the hurry of discussion and heat of controversy, he was suddenly summoned to eternity*.

* Two scarce volumes of the posthumous works of Lavoisier are extant, consisting, in great measure, of extracts from, and sketches of, his different papers read before the Royal Academy of Sciences; but several original Observations and Essays are also dispersed among them. They, in some degree, justify the observations which I have made in the text, that, had Lavoisier lived, he would have done merited justice to his predecessors and contemporaries, for he candidly reviews their opinions, and compares them with his own; at the same time, the following passage cannot be regarded as perfectly candid towards Rey, who, as I have shown above, founded his arguments, not upon hypothesis, but upon experiment.

I insert a long quotation, that there may be no misunderstanding upon the subject.

After stating the prevailing phlogistic notions entertained at that period, he proceeds as follows:—"Tel étoit l'état des connoissances, lorsqu'une suite d'expériences, entreprises en 1772 sur les différentes espèces d'air, ou de gaz qui se dégagent dans les effervescences et dans un grand nombre d'opérations chimiques, me firent connoître, d'une manière démonstrative, quelle étoit la cause de l'augmentation de poids, qu'acquîèrent les métaux lorsqu'on les expose à l'action du feu. J'ignoreis alors ce que Jean Rey avoit écrit à ce sujet en 1630; et quand je l'aurois connu, je n'aurois pu regarder son opinion à cet égard, que comme une assertion vague, propre à faire honneur au génie de l'auteur, mais qui ne dispensait pas les chimistes de constater la vérité de son opinion par des expériences. J'étois jeune, j'étois nouvellement entré dans la carrière des sciences, j'étois avide de gloire, et je crus devoir prendre quelques précautions pour m'assurer la propriété de ma découverte. Il y avoit à cette époque, une correspondance habituelle entre les savans de France et ceux d'Angleterre; il regnoit entre les deux nations, une sorte de rivalité qui donnoit de l'importance aux expériences nouvelles, et que portoit quelquefois les écrivains de l'une ou de l'autre nation, à les contester à leur véritable auteur; je crus donc devoir déposer, le 1^{er} Novembre, 1772, l'écrit suivant cacheté,

entre les mains du Secrétaire de l'Académie. "Ce dépôt a été ouvert à la séance du 5^{me} Mai suivant, et mention du tout a été faite en tête de l'écrit. Il étoit conçu en ces termes:—

"Il y a environ huit jours que j'ai découvert, que le soufre en brûlant, loin de perdre de son poids, en acquîeroit au contraire; c'est à dire, que d'une livre de soufre on pouvoit retirer beaucoup plus d'une livre d'acide vitriolique, abstraction faite de l'humidité de l'air; il en est du même du phosphore: cette augmentation de poids vient d'une quantité prodigieuse d'air qui se fixe pendant la combustion, et qui se combine avec les vapeurs.

"Cette découverte que j'ai constatée par des expériences que je regarde comme décisives, m'a fait penser que ce qui s'observoit dans la combustion du soufre et du phosphore, pouvoit bien avoir lieu à l'égard de tous les corps qui acquîèrent du poids par la combustion et la calcination: et je me suis persuadé, que l'augmentation de poids des *chaux* métalliques, tenoit à la même cause. L'expérience a complètement confirmé mes conjectures: j'ai fait la réduction de la litharge dans des vaisseaux fermés, avec l'appareil de Hales, et j'ai observé, qu'il se dégageoit, au moment du passage de la *chaux* en métal, une quantité considérable d'air, et que cet air formoit un volume au moins mille fois plus grand que la quantité de litharge employée. Cette découverte me paroissant une des plus intéressantes qui aient été faite depuis Stahl, j'ai cru devoir m'en assurer la propriété, en faisant le présent dépôt entre les mains du Secrétaire de l'Académie, pour demeurer secret jusqu'au moment où je publierai mes expériences."

(Signé)

"LAVOISIER."

"En rapprochant cette première notice de celle que j'avois déposée à l'Académie le 20^{me} Octobre précédent, sur la combustion du phosphore, du mémoire que j'ai lu à l'Académie à sa séance publique de Pâques 1773, enfin, de ceux que j'ai successivement publiés, il est aisé de voir, que j'avois conçu dès 1772, tout l'ensemble du système que j'ai publié depuis sur la combustion. Cette théorie à laquelle j'ai donné de nombreux développemens en 1777, et que j'ai porté,

Although LAVOISIER made few original discoveries, his talents were perhaps more usefully employed in setting forth and elucidating the researches of others, a task which he performed with great skill and success: in reviewing hypotheses, he diligently contrasts them with facts; weight and measure, which had been introduced into chemistry by BERGMAN, were strictly insisted upon in all his manipulations, and in his hands chemistry assumed the features of a new branch of knowledge, and put on its present character.

Connected with the labours of LAVOISIER is the celebrated reform of *chemical nomenclature* effected by him and his associates, among the most eminent of whom we may enumerate GUYTON MORVEAU*, FOURCROY†, and CHAPTAL‡. The former, amidst varied occupations, pursued

presque dès cette époque à l'état où elle est aujourd'hui, n'a commencé à être enseignée par Fourcroy, que dans l'hiver de 1786 à 1787; elle n'a été adoptée par Guyton Morveau, qu'à une époque postérieure: enfin, en 1785 Berthollet écrivait encore dans le système du phlogistique. Cette théorie n'est donc pas, comme je l'entends dire, la théorie des Chimistes François: elle est la mienne, et c'est une propriété que je réclame auprès de mes contemporains et de la postérité."

* Born at Dijon, 1737; died, 1815. "Guyton Morveau," says Davy, "was very old when I made his acquaintance; between seventy and eighty, and very feeble. Though he had been a violent republican, he was Bonaparte's director of the mint, and a baron of the empire. His manners were mild and conciliatory; and it is a proof of the energy of his mind, that having promised his vote to a person, as Corresponding Member of the Institute, he kept his promise, and my election wanted only his voice to be unanimous. Having never, when in France, inquired into the intrigues connected with elections, or interested myself about them, I should not have known this had he not himself told me so when I dined afterwards at his house."

—*Davy's Life*, by Dr. JOHN DAVY.

† Born at Paris, 1755; died, 1809.

‡ I have extracted the following notice of Chaptal from the address of H. R. H. the Duke of Sussex, delivered at the Anniversary Meeting of the Royal Society, November 30, 1832:—

"Jean Antoine Chaptal, Comte de Chanteloup, was born in 1756, and died in April last, in the 76th year of his age. He was Professor of Chemistry at Montpellier before the Revolution, and was one of the most active cultivators of chemical science before that event, in conjunction

with Monge, Fourcroy, Berthollet, Guyton de Morveau, and the illustrious Lavoisier. In the year 1793, upon the threatened invasion of France by the Allies, when saltpetre was not to be procured in sufficient quantities for the manufacture of the powder wanted by the French armies, he was invited by the Committee of Public Safety to superintend the establishments for that purpose; and his chemical knowledge so greatly improved the method followed in its manufacture, as in a very short time to make the produce greatly exceed the demand. He was made *Ministre de l'Intérieur* by Napoleon, and continued under the Empire to fill many important situations. He was the author of considerable works on chemistry, on the application of chemistry to the arts, on the application of chemistry to agriculture, on the art of making wines, and on the art of dyeing cotton and wool, which are written in a very perspicuous and elegant style, and which have enjoyed a very considerable popularity in France. The labours of his whole life, in fact, were devoted to the improvement of those manufactures whose perfection depended more or less upon the most correct and economical application of chemical principles; and, after his distinguished countryman, Berthollet, he must be placed in the first rank of those who have benefited the arts through the medium of chemical science."

"Chaptal," says Sir H. Davy, "for a long while Bonaparte's Minister of the Interior, was an active, amusing, intriguing courtier and chemist, and somewhat acquainted with the state of the chemical arts in France. Not very exact in conversation, and a little boasting, yet good natured, and with lively man-

chemistry with successful diligence, and, had he given nothing else to the science, his name deserves to be transmitted to posterity, as the inventor of the means of destroying infection by acid vapours, the efficacy of which he first pointed out in the year 1773. His first essay on the reform of nomenclature was published in the *Journal de Physique* for May, 1782, and although it was strenuously opposed by the colossal power of the Royal Academy of Paris, the plan was not only afterwards approved, but prosecuted by the eminent chemists of that metropolis. The different papers and correspondence relating to this subject are, in many respects, curious and interesting, from the difference of opinion which prevailed respecting the terms he adopted, and the ultimate benefit likely to result from the reformation. FOURCROY is a well-known name in the chemical world; his works rank among the most celebrated which France has produced in the science: he is the first author who published a *System* of chemistry. CHAPTAL was a successful contributor to the Chemistry of the Arts.

The difficulties attending an entire reform in the nomenclature of chemical science may be well imagined; they were encountered with considerable address; and it must be confessed, that, while it particularly tended to the dissemination of the anti-phlogistic doctrines, it facilitated the general acquisition of the science; the ludicrous terms of the alchemists were rejected, and names founded upon the nature of compound bodies, and upon the leading qualities of elementary substances, became their more sensible substitutes. It is true, that the progress of science has rendered much of the French nomenclature objectionable, and that it has been requisite to modify many of its terms, more especially such as were founded on erroneous theory: others, though objectionable, have been retained, rather than submit to the serious inconvenience to which repeated innovations tend; and nothing short of absolute necessity can justify us in changing old and accepted terms for those of more recent coinage. In the selection of names necessarily new, some leading and obvious property, independent of theory, should be selected as their basis; such terms as *iodine*, *bromine*, and *chlorine*, are in this respect unexceptionable. To the subjoined opinion upon this subject, by Sir H. DAVY*, I entirely subscribe:—

“Simplicity and precision ought to be the characteristics of a scientific nomenclature; words should signify things, or the analogies of things, and not opinions. If all the elements were certainly known, the principle adopted by LAVOISIER would have possessed an admirable application; but a substance in one age supposed to be simple, in another is proved to be compound; and *vice versâ*. A theoretical nomenclature is liable to continued alteration; *oxygenated muriatic acid* is as improper a name as *dephlogisticated marine acid*. Every school believes itself in the right; and if every school assumes to itself the liberty of altering the names of chemical substances, in consequence of new ideas of their composition or

ners, and quiet and ready conversation. More a man of the world than any of the savants of his day in France. It is said that he was author of Napoleon's decrees aimed at the commerce of England; if

so, he has contributed more than any other individual, except his master, to the military glory of the modern Briton.”

* *Elements of Chemical Philosophy*, pp. 46, 47.

decomposition, there can be no permanency in the language of the science; it must always be confused and uncertain. Bodies, which are similar to each other, should always be classed together; and there is a presumption that their composition is analogous. Metals, earths, alkalies, are appropriate names for the bodies they represent, and independent of all speculative views; whereas, oxides, sulphurets, and muriates, are terms founded upon opinions of the composition of bodies, some of which have been already found erroneous. The least dangerous mode of giving a systematic form to a language seems to be to signify the analogies of substances by some common sign affixed to the beginning, or the termination of the word. Thus, as the metals have been distinguished by a termination in *um*, as *aurum*, so their calciform, or oxidated state, might have been denoted by a termination in *a*, as *aura*; and no progress, however great, in the science, could render it necessary that such a mode of appellation should be changed. Moreover, the principle of a composite nomenclature must always be very limited. It is scarcely possible to represent bodies consisting of five or six elements in this way, and yet it is in such difficult cases that a name implying a chemical truth would be most useful."

Among the causes that have contributed to the recent progress of chemical science, we have already had occasion to advert to the *doctrine of definite proportionals*, which has enabled us to submit many of the phenomena of chemistry to calculation, and which promises to elucidate some of its most abstruse parts upon mathematical principles; but the chief source of the rapid advancement of chemistry during the present age, is doubtless the discovery of *the relation of electrical to chemical changes*; a discovery which has unfolded entirely new views of the mutual agencies of bodies, and which has equally furnished the theoretical and practical chemist with materials for speculative and experimental inquiry.

The curious experiments of GALVANI upon the convulsions excited in the limbs of animals, by the application of certain metals to their muscular and nervous fibres, led VOLTA to investigate the cause of such phenomena, and to attempt the accumulation of the electricity, to which he suspected they were to be referred: this he attained by successive alternations of different metals with substances acting chemically upon one of them; and he found that the extremities of such a pile were in opposite electrical states, and that the intensity of the electricity augmented the number of alternations. This instrument has been productive of vast discoveries, which are yet far from exhausted, and has given rise, in the hands of DAVY, to a new and curious department of chemical philosophy, into the history of which I shall enter a little more in detail, chiefly with a view of showing the singular talent and sagacity with which a difficult and intricate branch of science was successfully pursued and illustrated by that eminent individual.

It appears, from the "*additional observations*," appended to his *Chemical Researches, upon Nitrous Oxide, &c.*, published in 1800, that Sir H. DAVY had no sooner heard of VOLTA's researches, than his mind was awakened to their bearings upon chemical changes; and from that period, to the time of his first publication upon the subject, he seems not to have lost sight of the inquiry; indeed it was his characteristic habit

to examine without delay all novel results of other philosophers, and when he had confirmed their accuracy, he generally rendered them subservient to further discovery. Accordingly, we find that the first paper which he presented to the Royal Society (read the 18th of June, 1801,) was "*An Account of some Galvanic Combinations formed by the Arrangement of single metallic Plates and Fluids, analogous to the Galvanic Apparatus of Volta,*" and it contains several curious and interesting facts upon a subject which now began to excite general attention, and attracted the notice of many skilful experimentalists. The first harvest of fame, however, in this field of inquiry, was reserved for DAVY; and the *Bakerian Lecture* for 1806 contains a series of propositions and experiments, in reference to the chemical agencies of electricity, which at once display the masterly energies of the author's mind in passing from experiment to theory, and in the employment of that theory as the source of new, profound, and elaborate researches. About the time this paper was published, a great and important question respecting the agencies of electricity was undecided; it was not known whether electricity had the power of *generating* certain forms of matter, or whether they were merely *elicited*, by its influence, from compounds which escaped common modes of detection. Water, for instance, was found not merely to be resolved into its ultimate gaseous components, but their evolution was constantly connected with the appearance of acid and alkaline matter, and *that*, although every precaution was apparently taken to exclude foreign matters and all sources of impurity. Hence it was imagined that water either contained the elements of these bodies, or that it produced them by uniting with the electric fluids, or that they were actually conveyed, by some mysterious route, from the cells of the pile; indeed, it would be useless to enumerate all the speculations originating in these paradoxical phenomena; but it will be profitable to glance at the manner in which the difficulties were encountered by our author. He first repeated all that had been done by others, and criticized and compared their proceedings; he then electrized distilled water, and found, as they had found, the evolution of saline, alkaline, and acid bodies; but he also found that the more rigidly he purified the water, the smaller was the evolution of these products; a fact militating against their supposed source; still, however, they made their appearance. He now directed his attention to the vessels which were used, and succeeded in referring to *them* several extraneous bodies; thus glass, porcelain, and several mineral substances, yielded more or less foreign matter, which was successfully excluded when gold or platinum was substituted; but still, water, which had been redistilled at a low temperature in a silver alembic, did afford acid and alkali; the source of this was next traced to the hands of the operator, and the accidental contact of test-papers, all which were consequently avoided, with a proportionate diminution of the problematical appearances; but they were yet present, for notwithstanding all precautions, litmus was reddened in the positive, and turmeric rendered brown in the negative vessel: it was now, however, found that the acid and alkali were nitric acid and ammonia; substances producible by new arrangements of the elements of air and water; and accordingly when very pure water, carefully deprived, and kept from the contact, of air, was electrized *in vacuo*,

in cones of *gold*, which had not been *handled*, nothing but oxygen and hydrogen were elicited from it.

The question, therefore, concerning the origin of the appearances cited, was now so far satisfactorily determined. He then entered into many valuable contingent inquiries, and proves this essential fact, that electricity has the power not merely of rendering evident the smallest traces of foreign matter, but of decomposing compounds with apparent facility and perfection, the elements of which are held together by the strongest chemical attractive force; whence it was concluded that substances, hitherto deemed simple or elementary, might, under this all-powerful decomposing agent, afford evidence of a compound nature, and yield either known or new elementary bodies. The inquiry was accordingly resumed under this new light; and the Bakerian Lecture, read to the Royal Society, in November, 1807, contains the results to which it led. The first substances which occurred as likely to afford successful and novel information were the fixed alkalis. Upon subjecting caustic potassa to the action of the voltaic pile, it was found not to conduct electricity; and when its aqueous solution was used, the water only appeared to suffer decomposition. After several unsuccessful trials, it was at length found that the alkali, gently breathed upon, became sufficiently moist to suffer the transfer of electricity, and the appearances were very remarkable; effervescence ensued at the positive pole, and, at the negative, there appeared small and brilliant globules of a perfectly metallic appearance, but which presently burned upon exposure to air, and seemed to reproduce the alkali. There now could be little doubt that this matter was the *base* of potassa; but it became necessary to collect and preserve it for examination; and this was a task attended by many serious and apparently insurmountable obstacles, for the globules were successively immersed in a great variety of fluids, upon all of which they had more or less action, and none of which afforded a means of retaining them in a metallic state; at length the fluid called *naphtha* was successfully employed, and in it they were collected and preserved for a considerable time without material alteration. They were found truly metallic, eminently combustible, remarkably light, acting energetically and inflaming upon water, and producing potassa by their union with oxygen. Many of their other properties were also determined; and it here deserves especially to be mentioned, that although *potassium*, for so this new metal was called, was only obtained in minute atoms and a few grains in weight, all its essential properties, as subsequently determined, were correctly and minutely made out. *Sodium* was next obtained from soda by the same new method of decomposition; and shortly after the alkaline earths were shown to contain analogous inflammable and metallic bases. The *Philosophical Transactions* for several subsequent years contain continuations of these inquiries, which were actively and successfully pursued by their author, and which speedily attracting the admiration of the scientific world, induced others to resume and extend them.

In the year 1810 the subject of Sir HUMPHRY'S Bakerian Lecture is the "Oxymuriatic acid and its compounds," a subject which is pursued in several successive communications, abounding in original views and new discoveries. It is in these papers that the true nature of oxymuriatic

acid is demonstrated, that the views of SCHEELE respecting it are established, and that the erroneous reasoning regarding its composition, originating with BERTHOLLET, and sanctioned by the assent of the chemists of Europe, is refuted and subverted. Much acute reasoning, and many specimens of the true logic of the science, are to be found in these details, blended with sound descriptions of new compounds, and new applications of the facts that were developed : it is here that the nature of the muriatic acid is first demonstrated; that oxymuriatic acid (under the new name of *chlorine*) is shown to be an undecomposed substance; that a multiplicity of erroneous views respecting their compounds are corrected, and others established upon the basis of experiment, to the exclusion of hypothetical reasoning. The new theory to which these inquiries led was actively canvassed and opposed; but the objections urged against it necessarily yielded to the sound arguments and unequivocal experiments upon which it was founded, and the fame which the author acquired, by the gradual admission and general adoption of these new modes of reasoning and of research, was scarcely inferior to that which rewarded his more brilliant discovery of the alkaline bases. The several papers which follow this Lecture, and in which, among other subjects, the nature of *fluorine* and of *iodine* are discussed, may be considered as continuations and illustrations of the Bakerian Lecture, and they each contain further proofs of the inventive genius and talent of their author.

DAVY had now established himself as one of the first chemists of Europe: whether we found his claims to that distinction upon the number and importance of his original discoveries, or upon the profundity of his reasoning powers displayed in their applications, and stamping a peculiar character upon his inquiries. About this time he became desirous of embodying the results of his labours, and of displaying them in a more connected and systematic form, and, accordingly, in 1810, he published the first volume of his *Elements of Chemical Philosophy*, a work which, though it bears some marks of hasty composition, is abundant in evidence of the author's talent as an eloquent writer, a clear reasoner, and a shrewd and sagacious experimentalist. It is to be regretted that the second volume of this work never appeared; for although it be true that the first chiefly embraced those parts of the science which had been the particular objects of his successful studies, it cannot be doubted that his genius would have cast a new light upon the department of chemistry with which he was less immediately intimate. His *Elements of Agricultural Chemistry* appeared shortly after the *Chemical Philosophy*; it is a work containing some new and useful facts and views, and is well adapted to the capacities of those whom he intended to instruct.

Sir HUMPHRY had now laid a secure and deep foundation of permanent eminence and imperishable reputation as a chemical philosopher of the first class; but whilst he was thus employed, he was at the same time reaping equally verdant, though less durable laurels, as a lecturer; his style was peculiar and impressive; his eloquence powerful and appropriate; his experiments brilliant and original; his reasoning refined and acute. But to dwell further upon this subject would lead me to biographical particulars respecting his connexion with the Royal Institution,

and to details not immediately belonging to my present object, which I willingly, and, indeed, anxiously avoid, and turn with pleasure to his discovery of the SAFETY-LAMP.

The first paper in relation to this subject is printed in the *Philosophical Transactions* for 1815, and was followed by four communications bearing upon the same inquiry, the last of which was read to the Royal Society in January, 1817. These essays would alone characterize their author as a philosopher of no common stamp. Finding that flame would not recede through tubes of very small diameters, the idea occurred to him of constructing a lamp, the flame of which should have no connexion with the surrounding air, except by capillary tubes; and he inferred, from previous experiments, that such a lamp might safely be employed for the illumination of coal-mines infested with the explosive atmosphere commonly called *fire-damp*. He then endeavoured to ascertain the extent to which the tubes might be shortened without interfering with the principle of safety, and was thus led to cut them down till their transverse section became a series of fine meshes: this so closely resembled *wire-gauze*, that he was induced to try how far that tissue would prevent the passage of flame, and finding it effectual, he employed it in the construction of his lamp, and ultimately adopted the simple and efficient arrangement now in general and successful use. His researches respecting the nature of flame, and the temperatures at which combustion may, under various circumstances, be carried on, are parts of this general inquiry, and are not less ingenious than original.

Sir JOSEPH BANKS, who had been for so many years President of the Royal Society, died in June, 1820, and on the 30th of November following, Sir HUMPHRY DAVY succeeded to that high and honourable office. His *Discourses*, delivered on various occasions before that body, will give a fair idea of the general style of his eloquence and power in oratorical composition. He continued to contribute papers as heretofore, and some of them upon subjects of much interest, ably and philosophically discussed: among them, the essays on the modes of protecting the copper sheathing of ships deserve especial notice*.

In the course of the year 1827, Sir HUMPHRY'S general state of health became much impaired; he passed the greater part of the year 1828 in Italy, and terminated his memorable existence at Geneva, in May, 1829, in the fifty-second year of his age.

Of this eminent and extraordinary person two biographical memoirs have appeared, the one by Dr. PARIS, in 1831; and the other by his brother, Dr. JOHN DAVY, in 1836. Neither of these works will perhaps perfectly satisfy the *scientific* reader: they contain a variety of interesting and important matter, but are scarcely sufficiently ample in reference to those events in Sir HUMPHRY'S life, principally connected with his chemical pursuits, and his philosophical eminence. Dr. DAVY has, however, to a considerable extent filled this chasm in his brother's biography by the recent republication of his *Life*, in the form of a prefatory memoir to Sir HUMPHRY'S collected works. These volumes are a valuable addition to the philosophical literature of Europe, and furnish the chemical reader with a work of reference of great interest and usefulness.

* A list of Sir Humphry Davy's principal publications will be found at the end of Dr. Paris's work.

I became acquainted with Sir H. DAVY very soon after his arrival in London in 1801, having been introduced to him by Mr. HATCHETT, as a boy fond of chemistry: I was at that time at Westminster School, and often stole away upon a half holiday, to pass an occasional hour at the Royal Institution; soon afterwards I went abroad, and as soon as possible after my return, I renewed my acquaintance with Sir HUMPHRY; this acquaintance ripened into the friendship which so long subsisted between us, and which ultimately led to an event of which I shall always be justly proud, that of having been recommended by himself as a proper person to succeed him as Professor of Chemistry in the Royal Institution; to which office, after having delivered a probationary course of lectures during the preceding spring, I was unanimously elected on the 7th of June, 1813. From the time that Sir HUMPHRY quitted England for the Continent, in October, 1813, till his return in 1815, and during his subsequent visit in 1818, till his return in 1820, he regularly corresponded with me; and in the intermediate periods I was almost constantly in the enjoyment of his friendship and his society, or a witness and occasional assistant in his experimental labours in the laboratory of the Royal Institution.

From this correspondence I have selected three letters, which may, I think, be interesting, as relating to some of the points touched upon in the preceding paragraphs:—

My dear Sir,

Paris, December 11, 1813.

I SHALL enclose for the Royal Society a paper, containing results that, I think, will interest you. You will be so good as to give the paper to Sir Joseph as soon as you have perused it. I have sent him a copy, of which this is a duplicate. I wish that it may be read to the Royal Society as soon as possible. I transmit this copy to you, thinking that as you are preparing your Course, you will be glad to make an acquaintance with (iodine) a *fourth* supporter of combustion. Will you have the kindness to inform my brother with the contents of the paper; and request him to use some delicacy in communicating them to Dr. Hope, lest too great a shock should be given to the Professor, in finding the last hopes of oxymuriatic acid destroyed? I am only joking, for I know the Doctor is at the bottom too genuine a lover of science, and of truth, and of order, to preserve an arrangement which will have few advocates three months hence.

I leave Paris in a few days for Auvergne. You can write to me by the Transport Board on any matters of science, the letter being open, and sent under cover to Monsieur le Senateur Comte Real, Bureau de Police, Paris. Kind remembrances to all friends. Lady Davy desires her best compliments.

I am, my dear Sir, very sincerely yours,

Wm. T. Brande, Esq., Secretary to the Royal Society,
Royal Institution, 21, Albemarle Street, London.

H. DAVY.

His next letter is written soon after his arrival in Italy, in 1818*.

* The first paragraph relates to my marriage. I had previously received from him the following note, which I insert as a proof of the kindness of his feelings, and a specimen of his expression of them:

Venice, June 26, 1818.

My dear Sir,—Probably before you receive this letter you will be one of the happiest men in the world. You cannot be happier than I wish you to be: may you long enjoy all the best blessings that life can bestow, and health give relish to.

We have had a very prosperous journey here. The little scientific news there is, I have collected

in a letter to Sir Joseph Banks, which I am sure he will show you, and, therefore, will not tire you with repetitions.

Pray remember me, with the best wishes that can come from a friend, whose wishes are hopes for, and even perfect confidence in, your happiness, to her whom, in my next letter, I hope I shall have authority to call by your name.

I mention Trieste as the place where, if you will be so good as to write to me, I shall be sure of receiving your letter.

I am, my dear Sir,
very sincerely yours,

W. T. Brande, Esq.,
Royal Institution.

H. DAVY.

My dear Sir,

Idria, August 23, 1818.

I HOPE this letter will not arrive before you are not only *benedictus* but *beatus*; for if this word can at all apply to man in this mortal state, it is at such a time, and under such circumstances.

Since I wrote to you, at Vienna, we have made a very long journey. I have visited the most interesting parts of Hungary, Styria, Saltzbourg, and Carinthia, and have seen some mountain scenery quite as worthy of admiration as any I ever saw in the [Swiss Alps. I have lived amongst mountaineers purer and more uncorrupted than even the Swiss. We have had delightful weather, and have had full enjoyment of summer, fine but not sultry, in districts where, without fine weather, there could have been but little pleasure.

I will not write a geological letter, or describe to you the great calcareous mountain-chain that runs from Kevnoud, in Hungary, to Berchtesgarten in Bavaria, and to the centre of Carniola, with its belts of breccia, its intersections of schist, and its central column of granite. * * * * But I will give you a line on the *quicksilver mines*, which I came here to see. The formation is in bituminous schist, which sometimes emits inflammable air, and which alternates with limestone, like the Derbyshire. I have this day been down 1120 feet, and returned without being *salivated*. I pity the poor workmen, who all lose their teeth in a very short time. The veins of cinnabar are very beautiful; and one I saw nearly a foot in thickness. My wife went down with me, and visited the whole mine, which is rather a feat to be talked of for a lady.

I found a good deal of inflammable air (Carburetted Hydrogen) in the great salt-mine at Helstedt; the salt, like the quicksilver here, is in bituminous schist. I taught them the use of the lamp, which, notwithstanding the science of their imperial proprietor, they were still unacquainted with. A good many men had been burned a few months ago. The inflammable air is found in largest quantities where the *blue salt* is. I have been again searching in vain for the cause of this extraordinary colour.

I sent, in a letter to Mr. Hatchett, a little of Professor West's new metal, *Sirium*: I doubt its being a simple substance; perhaps you will try a few experiments upon it. I believe I mentioned to you, in my last letter, Count Stadion's *Oxychloric acid*; a very curious substance, very like sulphuric acid, and containing much more oxygen than Gay Lussac's acid. I have used detonating powder for Rivière's gun, made with the *oxychlorate* of Potassa, to use Stadion's name, and it answers perfectly. I am now in the *Proteus* country, and hope to send Sir Everard Home some alive; I go to the caverns where they are found, the day after tomorrow. I have seen nothing, and heard nothing, from England for two months. Pray address to me, Rome. I shall probably be there by the middle of October, on our way to Naples.

With every kind wish for your happiness, and that of her most dear to you, in which my wife joins me,

I am, my dear Sir, very sincerely yours,

H. DAVY.

Wm. Thos. Brande, Esq., Sec., R.S.

Royal Institution, Albemarle Street, London.

The third letter was written shortly previous to his return to England, and to the death of Sir JOSEPH BANKS, who expired at his villa at Spring Grove, near Isleworth, on the 19th of June, 1820.

Hotel de la Paix, Rue de la Paix, Paris, May 20, 1820.

My dear Sir,

It is long since I have written to you, but unless I have something to communicate, I do not like to trouble my friends; and in Italy, unless I rung changes upon my own small stock of scientific results, I had nothing to state in the way of chemical or philosophical information.

Here, there is little going on which you will not have seen noticed in the journals. A subject which seems to awaken much attention, is the increase of temperature of the surface of the globe, at considerable depths. If the results can be depended on, and are not influenced by accidental causes, the geometricians say they prove that at a few miles below the surface, the interior must be intensely hot; of a tempera-

ture far beyond that produced in any of our artificial operations. The subject is, at all events, a very curious one, and, in its geological relations, worth a very minute investigation.

Lord and Lady Spencer are here, and will be here for some time: they this morning gave me a piece of news which I hope is incorrect, but which makes us all very uneasy: it is that Sir Joseph is going to resign the chair of the Royal Society. * * * * * Pray write me a few lines, to tell me if this be true. Feeling very much interested in the progress of science in Great Britain, and in the dignity of scientific men, and of the Royal Society, I shall deeply regret such a measure, if it be in contemplation, * * * * * From the way in which Lord Spencer expressed himself, I have no doubt he would accept the chair; at the same time, I did not put the question to him, but Lord Spencer, or * * * * * would give dignity to the situation; and scientific *Vice Presidents*, might keep alive the scientific character of the body. * * * * * Pray write to me by return of post upon this subject, which I think is almost a *national one*.

I am much obliged to you for your *Manual*, which is the best collection and arrangement of chemical science existing. I have given the only copy I have received to Sementini, who is going to publish immediately an Italian translation of it. I preferred making it subservient to the progress of science, to keeping it for my own gratification. Lady Davy joins me in kind remembrances to Mrs. Brande.

Believe me to be, my dear sir, very sincerely yours,

Wm. Brande, Esq., Sec. R. S., &c.

H. DAVY.

Royal Institution, Albemarle Street, London.

Of Sir HUMPHRY's latter days, the following particulars are extracted from the interesting narrative of his friend and physician, Dr. TOBIN, who accompanied him on his last journey into Italy, and was with him till his death. Dr. TOBIN says, that on his arrival in London, March 26, 1828, he found Sir HUMPHRY much altered during the four years which had elapsed since he last saw him, and it was evident that although his mind was still vigorous and full of energy, his bodily infirmities pressed heavily upon him. On the morning of the 29th of March, he left his house in Park Street, Grosvenor Square, for Dover, crossed next day to Calais, and then proceeded up the Rhine, and through Styria and Carniola, into Italy. He arrived at Rome on the 18th of November, without any remarkable change in his health. And, as it appears from Dr. TOBIN's narrative, that he frequently was occupied during the greater part of the day in fly-fishing and shooting, his corporeal strength must have been considerable. He, however, shunned society, and passed his evenings, and such days as he kept the house, in being read to, and in playing at *écarté*, and in dictating his *Vision*. In his diary, for instance, on the 31st of December, 1828, Dr. TOBIN says, "Our daily life has hitherto been as monotonous as possible. Sir Humphry sees no society, and wishes to see none, and his only pleasure and amusement seems to consist in shooting. He drives out every day in the surrounding *Campagna*, often to a distance of twelve and fourteen miles from Rome, when he gets out, and rides on his pony over the fields in search of quails or snipes. On his return, when he is not too much fatigued, he dictates to me a continuation of his *Vision*, which he thinks of forming into a series of dialogues on religion and other subjects; and our evenings are spent as they have been ever since we left Calais, with a game or two at cards, and with my reading to him different works, principally English and French, which he procures from a circulating library in the Corso. I have formed no acquaintances, as Sir Humphry wishes me not to do so;

but when I have copied off the morning's dictation, I often take a solitary walk in the garden of the Pincio, to St. Peter's, or to the Colosseum."—(TOBIN'S *Journal*, p. 196.)

On the 20th of February, 1829, Sir H. DAVY was attacked with a renewed stroke of palsy*, which had nearly proved fatal, and which induced Dr. TOBIN to write to Dr. DAVY at Malta, and to Lady DAVY in London; the former arrived at Rome on the 15th of March, and the latter on the 30th. By this time Sir HUMPHRY had considerably regained the power over his limbs, and was able to lie upon the sofa the greater part of the day. "It seems impossible," says Dr. TOBIN, "for him to exist without being read to, and on one day I read Shakspeare to him for *nine* hours."

On the 30th of April, Sir HUMPHRY, now accompanied by his wife and brother, left Rome, and passing through Sienna, Florence, Genoa, and Turin, over Mount Cenis, reached Geneva on the 28th of May; on the 29th, the following is recorded in Dr. TOBIN'S *Diary*. "I quitted Sir Humphry yesterday evening, after having read to him as usual till about ten o'clock. Our book was Smollett's *Humphrey Clinker*, and little did I think it was the last book he would ever listen to. He seemed in tolerable spirits, but upon going to bed was seized with spasms, which, however, were not violent, and soon ceased. I left him when in bed, and bidding me "good night," he said I should see him better in the morning. Lady Davy and the Doctor also quitted him, and George (his servant) went to bed in his master's room, as he always had done since Sir Humphry's illness at Rome. At six o'clock this morning, Lady Davy's man-servant came to my room, and told me that Sir Humphry was no more! I replied that it was impossible, and that he probably only lay in a torpor; but I went down to his room instantly, when I found that the servant's words were, alas! but too true. I asked George why he had not called me, when he said, that he had sent up, but now found that it had been to a wrong room. He told me that Sir Humphry went to sleep after we had left him, but that he twice waked, and that at half-past one, hearing him get out of bed, he went to him, when Sir Humphry said he did not want his assistance, and poured some solution of acetate of morphine into a wine-glass of water; but this still remained untouched upon his table. George then helped him into bed, where, he says, he lay quite still till a little after two o'clock, when hearing him groan, he went to him, and found that he was senseless and expiring. He instantly called up Lady Davy and the Doctor, and sent up, as he believed, to me; but Sir Humphry, he says, never spoke again, and expired without a sigh.

"I had so often, whilst at Rome, seen Sir Humphry lie for hours together in a state of torpor, and to all appearance dead, that it was

* The first symptoms of this disease seem to have alarmed him in the year 1826, and to have appeared after his exertions on the 30th of November in that year, on which occasion he delivered his last discourse, at the anniversary meeting of the Royal Society; and some weeks afterwards, whilst upon a shooting excursion with Lord Gage, in Sussex, he was seized with a more alarming attack, from the immediate effects of which he however soon rallied.

difficult for me to persuade myself of the truth; but the delusion at length vanished, and it became too evident that all that remained before me of this great philosopher, was merely the cold and senseless frame with which he had worked. The animating spirit had fled to its oft self-imagined planetary world, there to join the rejoicing souls of the great and good of past ages, soaring from system to system, and with them still to do good in a higher and less bounded sphere, and I knew that it was freed from many a wearisome and painful toil. Yet I could not look upon Sir Humphry as he was, without remembering that which he had been, and my tears would fall, spite of my effort to restrain them."

The following memorandum, relating to the last hours of his brother's life, is given by Dr. DAVY, (*Memoirs*, vol. ii., p. 365.) "On the 28th of May, 1829, we arrived at Geneva: at five, he dined at table and made a tolerable dinner; after dinner he was read to, according to custom. At nine o'clock, he proposed to go to bed. In undressing, he struck his elbow against the projecting arm of the sofa on which he sat: the effect was very extraordinary; he was suddenly seized with an universal tremor; he experienced intense pain in the part struck, and a sensation, he said, as if he were dying. He was got into bed as soon as possible. The painful sensations quickly subsided, and in a few minutes were entirely gone. There was no mark of hurt on the elbow, no pain, or remaining tenderness; and the effect of the blow perplexed him no less than it did me: a slight feverish feeling followed, which he thought little of; he took an anodyne draught of acetate of morphia, and then desired to be read to, that he might be composed to sleep by agreeable images.

"About half-past nine he wished to be left alone, and I took my leave of him for the night, and for ever on earth. His servant, who always slept in his room, called me about half-past two, saying he was taken very ill. I went to him immediately; he was then in a state of insensibility; his respiration extremely slow and convulsive, and the pulse imperceptible: he was dying; and in a few minutes he expired. I thank God I was present to close his eyes. In death, his countenance was composed, and of its mildest expression, indicative of no pain or suffering in the separation of the immortal from the mortal part. This fatal moment was about three, A.M., on the 29th of May." His remains were deposited on the 1st of June in the burying-ground, without the walls of Geneva, and close to the grave of Professor PICTET.

The theory of definite proportionals was adopted and illustrated by Sir H. DAVY, and his *Elements* is the first publication in which it was generally applied. This theory received, about the same time, extensive elucidation at the hands of M. GAY LUSSAC, but its promulgation in this country is chiefly to be attributed to Dr. WOLLASTON, whose admirable suggestion of a synoptic scale of chemical equivalents, already referred to, was brought before the Royal Society in November, 1813. Many years previous to this he had established the important doctrine of multiple proportions, in a paper "On Super-acid and Sub-acid Salts," printed in the *Philosophical Transactions* for the year 1808: he now showed the important practical applications of which the theory was susceptible, and

by connecting the scale of equivalents with GUNTER'S sliding rule, has put into the hands of the chemist an instrument infinite in its uses, and equally essential to the student, the adept, and the manufacturer.

Dr. WOLLASTON'S first contribution to the Transactions of the Royal Society was in June, 1797, being an essay *On Gouty and Urinous Concretions*, in which he made known several new compounds connected with the production of those maladies, in addition to the uric combinations previously discovered by SCHEELE: these were, Phosphate of Lime; Ammonia-magnesian Phosphate; a mixture of the two forming the *fusible Calculus*; Oxalate of Lime; and, more lately, he added Cystic Oxide to the list of his previous discoveries. (*Phil. Trans.*, 1810.) In 1804 and 1805, he made known Palladium and Rhodium, two new metals contained in the ore of platinum, and associated with Osmium and Iridium, discovered about the same time by Mr. TENNANT. In 1809, he showed that the supposed new metal, Tantalum, was identical with Columbium, previously discovered by Mr. HATCHETT; and shortly before his death, which happened on the 22d of December, 1828, in the sixty-third year of his age, he transmitted to the Royal Society the *Bakerian Lecture*, in which he fully describes his ingenious method of rendering platinum malleable.

Dr. WOLLASTON made a few other chemical communications to the Royal Society, but his papers are chiefly on subjects more immediately connected with physical and physiological inquiries; they are all remarkable for the singular and satisfactory simplicity of his experimental methods, for the perspicuity of his theoretical deductions, and for the extreme caution with which he touches upon generalizations and hypothesis. His uncommon tact, neatness, and dexterity as an experimental chemist, will never be forgotten by those who had an opportunity of witnessing his performance of any analytical operation; he practised a peculiar method of microscopic research, in which he willingly instructed those who asked his information; and we owe to him numerous abbreviations of tedious processes, and a variety of improvements in the application of tests, which have gradually become public property, although he never could be induced to describe his manipulations in print, or to communicate to the world his happy and peculiar contrivances.

Of Dr. WOLLASTON, (who was born at East Dereham, in Norfolk, on the sixth of August, 1766,) I am afraid no authentic biography has as yet appeared: the following are a few memoranda respecting his last illness, which were obtained from conversation, at the time, with some of his intimate friends.

In October, 1827, while accompanying a friend to Cashibury, the seat of the Earl of Essex, he spoke of a numbness which he had for some time felt in his left arm, and which he stated he considered as a symptom of paralysis, a disease to which his father and eldest brother had fallen victims, and of which, at a subsequent period, another brother also died. In June, 1828, while on a fishing excursion at Stockbridge, feeling some stronger premonitory indications of a paralytic seizure, he abruptly quitted his amusement, and returned to London. In July of the same year, while on a visit to the late Earl Spencer, at the Isle of Wight, he noticed that a part of the retina of his left eye had become insensible to the

action of light. In the month of September, he went upon a shooting excursion to Mr. WHITBREAD's in Bedfordshire, where he remained eight days, and enjoyed his sport: one evening he jokingly said, "For the first time in my life I count my game by the quarter of a hundred," having killed twenty-five head. He returned home better in health, but soon after, the sensation in his arm became worse, and whilst staying with Mr. BLAKE in Hertfordshire, he felt so unwell and uncomfortable as to be obliged to return home a day or two earlier than he intended. In the course of the following week, symptoms more decidedly alarming came on; the use of his arm was much impaired, and the muscles of the face and organs of speech were affected: his mental faculties, however, remained entire to the last. He was sedulously attended by several medical friends, and especially by Dr. JAMES SOMERVILLE, who remained in the house during his illness and until his death.

The loss of two such men as WOLLASTON and DAVY, within so short a period, and scarcely beyond the prime of life, was a serious national calamity: the sketch which I have given of their labours is a most imperfect outline; but it would have been improper and indecorous to have dismissed this brief History of Chemistry without such notice, and I shall conclude with the following delineation of their intellectual portraits, for which we are indebted to the late Dr. HENRY. (*Elem. of Chem.*, 11th edit., viii.)

"To those high gifts of nature, which are the characteristics of genius, and which constitute its very essence, both those eminent men united an unwearied industry and zeal in research, and habits of accurate reasoning, without which even the energies of genius are inadequate to the achievement of great scientific designs. With these excellencies, common to both, they were nevertheless distinguishable by marked intellectual peculiarities. Bold, ardent, and enthusiastic, DAVY soared to greater heights; he commanded a wider horizon; and his keen vision penetrated to its utmost boundaries. His imagination, in the highest degree fertile and inventive, took a rapid and extensive range in pursuit of conjectural analogies, which he submitted to close and patient comparison with known facts, and tried by an appeal to ingenious and conclusive experiments. He was imbued with the spirit, and was a master in the practice, of the inductive logic; and he has left us some of the noblest examples of the efficacy of that great instrument of human reason in the discovery of truth. He applied it, not only to connect classes of facts of more limited extent and importance, but to develop great and comprehensive laws, which embrace phenomena that are almost universal to the natural world. In explaining those laws, he cast upon them the illumination of his own clear and vivid conceptions;—he felt an intense admiration of the beauty, order, and harmony, which are conspicuous in the perfect CHEMISTRY of NATURE;—and he expressed those feelings with a force of eloquence, which could issue only from a mind of the highest powers, and of the finest sensibilities. With much less enthusiasm from temperament, Dr. WOLLASTON was endowed with bodily senses of extraordinary acuteness and accuracy, and with great general vigour of understanding. Trained in the discipline of the exact sciences, he had acquired a powerful command over his attention, and had habituated himself to the most rigid correct-

ness, both of thought and language. He was sufficiently provided with the resources of the mathematics, to be enabled to pursue, with success, profound inquiries in mechanical and optical philosophy, the results of which enabled him to unfold the causes of phenomena, not before understood, and to enrich the arts, connected with those sciences, by the invention of ingenious and valuable instruments. In Chemistry, he was distinguished by the extreme nicety and delicacy of his observations; by the quickness and precision with which he marked resemblances, and discriminated differences; the sagacity with which he devised experiments, and anticipated their results; and the skill with which he executed the analysis of fragments of new substances, often so minute as to be scarcely perceptible by ordinary eyes. He was remarkable, too, for the caution, with which he advanced from facts to general conclusions; a caution which, if it sometimes prevented him from reaching at once to the most sublime truths, yet rendered every step of his ascent a secure station, from which it was easy to rise to higher and more enlarged inductions."

The talented author of the preceding paragraph is himself now amongst those who claim a place in this historical outline of the progress of chemical philosophy. In the address delivered at the Anniversary Meeting of the Royal Society, on the 30th November, 1836, the President says, "The last name which occurs in the melancholy list of our departed associates is that of Dr. WILLIAM HENRY, to whom the science of Chemistry generally, and of Gaseous Chemistry in particular, is under great obligations. He was the author of nine papers in our *Transactions*, many of them of great merit; and his *Elements of Chemistry* is one of the best-written and best-arranged compendiums of that important and extensive science which has been published of late years, whether in our own or in any other language. The *Memoirs* of the Manchester Society are chiefly indebted to him, in conjunction with Dr. DALTON, for the high character which they have so long maintained. Dr. HENRY, like Dr. WOLLASTON, made the results of science, obtained by the most original and difficult researches, the foundation of a splendid fortune; and few persons have contributed more effectually by their discoveries and exertions to the promotion of those arts and manufactures which form the foundation of the prosperity of a great commercial nation."

The chemical world has also sustained a serious loss in the death of Professor TURNER, of University College in this Metropolis. "Dr. EDWARD TURNER was a native of Jamaica, and studied medicine at Edinburgh, and chemistry at Göttingen, under the instructions of the celebrated analytic chemist, Stromeyer. He became a lecturer on chemistry at Edinburgh in 1824, and his first publication was a short introduction to the study of the laws of chemical combination and the atomic theory. He obtained the Professorship of Chemistry in University College, London, at its first establishment in 1828, a situation which he continued to hold to the end of his life. His *Elements of Chemistry* have enjoyed an uncommon degree of popularity, and are remarkable for clearness and precision, both in the description of his experiments and in the deduction of his theory. He was the author of two papers in the *Philosophical Transactions*, the first, "on the Composition of Chloride of Barium," and the second, containing "Researches on Atomic Weights," both written with

a view of impugning the theory, which had been promulgated by some English chemists of high authority, "that all atomic weights are simple multiples of that of hydrogen." In the year 1835, Dr. TURNER was compelled by the declining state of his health to suspend all original researches, confining himself simply to the duties of his Professorship, and he died in February, 1837, in the fortieth year of his age, to the deep regret of every friend of the progress of chemical science. He was a person of engaging manners and appearance, and of most amiable character; his body was followed to the grave with every manifestation of respect and affectionate attachment by the whole of the pupils and Professors of the Institution, of which he had so long been a principal ornament*."

* The above notice is extracted from the Anniversary Address of the President of the Royal Society on the 30th November, 1837. I had the pleasure of Dr. Turner's acquaintance, and can bear ample testimony to his excellence as a

man, and to his talent and industry as a teacher. Reference need only be made to his elementary work on Chemical Philosophy, to establish his merit as an author.

MANUAL OF CHEMISTRY.

CHAPTER I.

HOMOGENEOUS ATTRACTION. CRYSTALLIZATION.

It is the object of Chemistry to investigate the causes and effects of all changes in the constitution of matter, whether produced by heat, mixture, or other means. Its general range, therefore, is so extensive, and the individual cases requiring explanation so numerous, that *Arrangement* is of the utmost consequence to its successful study. In the present state of our knowledge, it will be found most convenient to begin with the discussions relating to the *general powers or properties of matter*, and afterwards to proceed to the examination of *individual substances*, and to the phenomena which they offer when presented to each other under circumstances favourable to the exertion of their mutual chemical agencies.

The powers and properties of matter, connected with chemical changes, may be considered under the heads of Homogeneous Attraction, or Aggregation; Heat; Light; Chemical Attraction, or Affinity; Electricity, and Magnetism.

§ 1.—ATTRACTION. AGGREGATION. CRYSTALLIZATION.

ATTRACTION may be regarded as acting at *sensible* and at *insensible* distances. In the former case, it is called *gravitation*. It is the power by which substances are propelled towards the earth; it exists in all known forms of matter; and it acts directly as the mass, and inversely as the square of the distance: restrained by *inertia*, it preserves the planetary bodies in their orbits, presides over their movements, and tends to confer upon the system of the universe that consummate harmony which the genius of Newton unveiled.

Attraction is also exerted at insensible distances, and among the minutest atoms of matter. It thus preserves the form, and modifies the texture of solids; gives a spherical figure to fluids; causes the adhesion of surfaces; and influences the mechanical characters of bodies. The different forces with which it is exerted are seen in the different *textures* of solid bodies, which are sometimes exceedingly hard and difficultly divisible, as the diamond, rock-crystal, &c. others are comparatively soft or brittle, and exhibit less intensity of aggregation, such as chalk and calcareous spar: and in others the power is so modified as to produce plasticity, porosity, elasticity, and tenacity, as seen in clay, sponge, caoutchouc, and iron wire.

As the results of gravitation are counteracted by those of inertia, so the influence of aggregation is opposed by a repulsive force, apparently due to the various agencies of *heat*; and it is probable that the various states or forms of matter are chiefly dependent upon the relative intensities of these antagonist forces. In *solids* aggregation predominates so as to prevent their particles freely moving upon each other; but in fluids they move upon each other with the utmost ease, and in some more readily than in others; hence their division into *liquids* or *inelastic fluids*, and *aëriform* or *elastic fluids*; the dimensions of the former are not materially influenced by pressure, and they were for a long time considered as absolutely incompressible; this, however, is not strictly true, although the force required to change their volume is very great, and the extent of the change very small. The following table shows the amount of compression of four liquids, deduced from the experiments of Oersted, in millionths of their volume, for each additional atmosphere.

Mercury	2.65	millionth parts.
Alcohol	21.65	"
Water	46.65	"
Ether	61.65	"

Mr. Daniell states that by plunging a vessel of water into the sea to a depth of 1000 fathoms, the compression amounts to one-twentieth of the bulk. In all cases after the pressure is withdrawn, the liquids reassume their original bulks. Aëriform or elastic fluids are indefinitely elastic and compressible, their volume, as was first accurately ascertained by Mariotte, being always inversely as the pressure. (See ATMOSPHERIC AIR.) The influences of *heat* upon the forms of matter will be fully discussed in the section upon that subject.

The mutual attraction between the surfaces of solids and liquids gives rise to the phenomena of *capillary attraction*, so called from its causing the visible rise of fluids in tubes of very small bore: thus, if a tube, with a capillary bore of one-fiftieth of an inch, be dipped at one end into a glass of water, the water rises to about $2\frac{1}{2}$ inches, and the rise is great in proportion to the smallness of the bore of the tube. If two plates of glass be so held as to form a very acute angle with each other, and the lower edges dipped into water, the liquid rises in the form of a curve (hyperbola) between the plates, rising highest where the space between them is least. It is in consequence of this species of attraction that a drop of water pressed upon a solid surface wets and adheres to it; and that the surface of the water in a tumbler is not truly level, but a little elevated upon the edges. These phenomena of capillary action depend upon the nature of the substances presented to each other; thus the water will not rise upon greasy glass, or wax; and hence also different liquids rise to different heights in the same tube, independent of their specific gravities, and of their relative degrees of viscosity; and mercury not only does not rise, but is depressed in the bore of a common glass tube: so that, unlike water, it presents a convex instead of a concave surface when poured into a glass, because in it the attraction of the particles of the mercury for each other is great, and they are not attracted by those of the glass; in other words, they are incapable of *wetting* it. "The mercury within the tube is cut off by the inactive surface of the

glass from the homogenous attraction of the surrounding mass; its own self-attractive force therefore acts as from its centre, drawing its particles together and causing them to assume more or less of a globular aggregation, according to the same law which determines the spheroidal form of a suspended drop of liquid."—See DANIELL'S *Introd.* 583. The rising of fluids in porous and spongy bodies, the ascent of oil or spirit in the wicks of lamps, the diffusion of moisture in the earth, and the distribution of the juices of plants, are a few of the important consequences of capillary attraction.

Mr. Daniell remarks, that the same adhesive attraction takes place also between solids and aëriform bodies, as illustrated by the following experiments. Sift some magnesia upon the surface of water, and it will presently sink to the bottom; sift in the same way some fine iron filings, and although their specific gravity is nearly four times greater than that of magnesia, and between seven and eight times greater than that of water, they float upon the surface and to such an extent, that a stratum of considerable thickness may be laid on the liquid; this at length sinks in considerable masses, when it is seen that they had been previously buoyed up by the adhesion of air, which their accumulated weight even carries with them to the bottom, the surface of each fragment of metal having been enfilmed with air, which prevented its being wetted by the water: in the case of the magnesia its attraction for air being less, it was more easily displaced by the water. The force of adhesion of air to glass has also been shown by Mr. Daniell to be very considerable, and to this cause he refers the gradual deterioration of barometers, by the creeping up of air between the mercury and the tube, an effect which he has ingeniously prevented by welding a ring of platinum to the bottom of the tube, which admits of the adhesion of, or being *wetted* by, the mercury, and so intercepts the air. The welding of the platinum to the hot glass is, he observes, a good instance of strong heterogeneous attraction.—(*Introd.* § 87.)

The adhesion of air to a liquid is shown by the quantity which escapes when water is poured from one vessel into another, the air attached to its surface being carried down by the momentum of the falling mass and again escaping in bubbles: the foam of water-falls results from the same cause, and it is thus that air gradually pervades masses of water, and tends to its entire aëration, so as to fit it for the respiration of aquatic animals. This air escapes under diminished pressure, and may be entirely expelled by long continued boiling. Many other phenomena connected with this subject will afterwards come before us.

The results of attraction, as relating to the shape and form of matter, are influenced by the circumstances under which it has taken place. Sometimes the particles are, as it were, indiscriminately collected: at others, they are beautifully arranged, producing regular and determinate figures; in this case, bodies of the same composition often affect the same form; hence we are not unfrequently enabled to infer the composition of a substance from accurate inspection of its external or mechanical characters. Absolute identity of form, however, is not necessarily associated with identity of composition, for certain substances may be substituted for each other in combination, without affecting the form of the com-

pound. Thus the arseniate and binarsenate of soda have the same forms as the phosphate and biphosphate of soda; and the arseniate and binarsenate of ammonia resemble the phosphate and biphosphate of that alkali. Professor Mitscherlich, (*Ann. de Chimie et Phys.*, tom. xiv. xix. xxiv.) to whom we owe these and other facts connected with the subject, which we shall consider afterwards, terms such salts *isomorphous*, and has shown that there is a remarkable analogy in the chemical arrangement of their constituents. Thus, in the above instances, the proportionals of acid, of base, and of water of crystallization, correspond; and he has traced a similar correspondence in the atomic constitution of the acids of the salts.

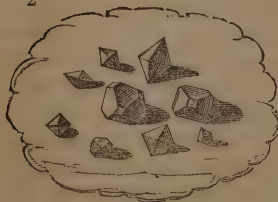
The regular polyhedral solids resulting from homogeneous attraction are usually called *crystals*; and the bodies are said to be susceptible of *crystallization*. To enable the particles of bodies to assume that regular form which crystals exhibit, it is obvious that they must have freedom of motion; and, accordingly, the first step towards obtaining a body in its crystalline form, is generally to confer upon it either the liquid or aëri-form state. The former is usually effected by solution in water, alcohol, or other liquids; the latter by exposure to heat.

When common salt is dissolved in water, its particles may be regarded as disposed at regular distances throughout the fluid; and if the quantity of water be considerable, the particles will be too far asunder to exert reciprocal attraction: in other words, they will be more powerfully attracted by the water than by each other. If we now slowly get rid of a portion of the water by evaporation, some of the saline particles will gradually approach each other, and they will aggregate according to certain laws, producing a regular solid of a *cubic form*; another portion of the salt will remain dissolved in the residuary water, which is usually called the *mother liquor* or *water*.

1



2



When crystallized substances are slowly acted upon by water, its influence is often curiously modified by the texture of the saline mass, (Daniell, *Quart. Journ.*, I.) If for instance, we take a shapeless lump of alum, and plunge it into a tumbler-ful of cold water, we shall observe that in a few days the surface of that salt will be eaten and carved out into a variety of regular forms, somewhat as represented in the annexed cut. If we now put a drop of the solution contained in the tumbler upon a plate of glass, we shall perceive, as the water slowly evaporates, that the particles of alum which it contained congregate into regular forms, which, when examined by a common pocket lens, appear as in fig. 2, and are small and beautifully formed eight-sided figures, or *octoëdra*. In this case the water is said to be the *solvent* of the alum, and the process by which it is obtained in regular forms or *crystals*, is called *crystallization*. In this

and similar instances, the crystals are liable to certain *modifications*; thus, among the little octoëdrons, to which we have adverted, it is not uncommon to find some, the angles of which are cut off, or *truncated*, or replaced by secondary surfaces; sometimes the edges too are similarly modified, and the crystals assume these figures:



Truncated Angles.

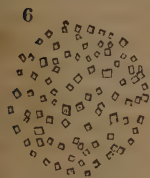


Truncated Edges.



Truncated Edges and Angles.

Most of the saline substances soluble in water may be thus exhibited in a crystalline form; and as each substance usually assumes a distinct figure, or is characterized by some obvious, and, at the same time, peculiar properties, we are often enabled to pronounce upon the chemical nature or composition of a body, by a careful examination of its crystalline forms; and such experiments are particularly neat and satisfactory, in consequence of their facility, and the small scale upon which they may be performed: for the figures of the smallest crystals obtained from a drop of their solution, resemble the large ones formed in gallons of it; and although, in collecting specimens of crystallized salts, it is convenient to have them large and perfect, the smallest ones that may be viewed through a microscope furnish the chemist with equally satisfactory evidence of the nature of the dissolved salt: for instance, put a tea-spoonful of common salt, nitre, Glauber's salt, and Epsom salt, into separate wine glasses: fill them up with water, and occasionally stir their contents to help the solution: when dissolved take a drop of the clear liquor, with a glass rod, out of each of the wine-glasses, and place them side by side upon a strip of clean plate-glass, which may be placed upon a chimney-piece, or somewhere very gently warmed. As the water evaporates, the salts will crystallize, and we shall observe the following figures appropriated to each: the common salt exhibits *cubes*; the Epsom salt, *four-sided prisms*; the nitre, *six-sided prisms*; the Glauber's salt, *striated six-sided prisms*.



Common Salt.



Epsom Salt.



Nitre.



Glauber's Salt.

The Glauber's salt and the nitre might possibly at first be mistaken for each other, but, while the latter remains unaltered by exposure to air, the former soon loses its transparency, and crumbles down into white powder. Salts which behave thus are said to *effloresce**: other salts,

* This property of efflorescence would appear in some cases to depend upon superficial fracture, for Mr. Faraday found that crystals of carbonate, phosphate, and sulphate of soda, having no parts of their surfaces broken, and carefully preserved from external violence, remained perfect; but upon breaking or scratching their surface efflorescence began at that part, and covered the whole.—*Phil. Trs.*, 1834, p. 74.

instead of thus spontaneously parting with a portion of their *water of crystallization*, attract moisture from the air, or *deliquesce*, as is the case with carbonate of potassa, acetate of potassa, chloride of calcium, &c.: alum and many other salts, although they contain water, do not thus part with it, and are *permanent* in the air. But water is not necessarily contained in all crystals: there is none, for instance, in nitre; and such are called *anhydrous salts**. Some salts require a high temperature to deprive them of water. This is the case with gypsum, or sulphate of lime, which is commonly found in large transparent crystals, permanent in the air; but at a red heat they lose one-fifth their weight of water, and crumble down into the white powder commonly called *plaster of Paris*, which is, therefore, an *anhydrous* sulphate of lime, and which, when mixed with a little water, again combines with it, and concretes in the act of combination; hence the use of this substance for forming casts or impressions, as seen in mouldings, busts, &c. Efflorescent salts may sometimes be conveniently preserved by slightly oiling their surfaces, or by soaking them for a few hours in olive oil, and then wiping them and putting them in bottles; or they may be kept under a glass shade in which is also included a small saucer of water. The action of heat upon salts is much influenced by their relative quantities of water of crystallization; it renders some of them, such as sulphate of soda, extremely fusible; from others the water evaporates before fusion, and occasions the efflorescence of the salt; and if contained in their pores, it causes them to *decrepitate*, or fly to pieces when heated, with a peculiar crackling; but this effect more generally depends upon the sudden expansion of the outer crust of the crystal, and its bad conducting power for heat.

10



Epsom Salt, or Sulphate of Magnesia.

11



Saltpetre, or Nitrate of Potassa.

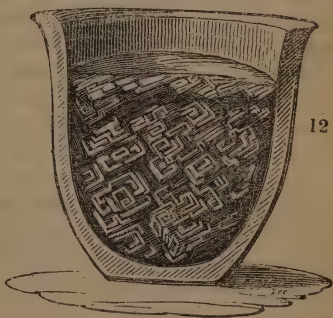
The regularity of the figures of crystals will be influenced by the rapidity of the evaporation; if the process be slowly conducted, the particles unite with great regularity; if hurried, the crystals are irregular and confused. Loaf-sugar and sugar-candy furnish good instances of such modifications. The former being the result of rapid, the latter of slow, crystallization. In common cases, the evaporation may be continued till a *pellicle* forms upon the surface of the solution, which indicates that the attraction of the saline particles for each other is becoming superior to their attraction for the water. The formation,

* *Anhydrous* is a term derived from the Greek, signifying *without water*.

therefore, of a superficial pellicle is the common criterion of the fitness of a solution for crystallization; but where the object is to obtain very regular and very large crystals, the evaporation must be much slower, and carried to much less extent; even *spontaneous evaporation*, or that which takes place at common temperatures, must be resorted to.

It is in this way that the gigantic crystals of sulphate of magnesia and of nitrate of potassa, represented in figs. 10 and 11, were procured; they are here inserted to show the size and perfection of crystals thus slowly deposited in large quantities of their solutions, as contrasted with the microscopic forms described above.

There are certain bodies which may be dissolved or liquified by heat, and, during slow cooling, may be made to crystallize. This is the case with many of the metals; and among them bismuth furnishes, when carefully managed, the most beautiful results; for this purpose a few pounds of it should be melted in a deep iron ladle or crucible, and, as soon as the surface has concentered, it should be punctured with a pointed iron rod, and the liquid metal immediately poured out from the interior; on cautiously breaking the hollow ingot thus obtained, the interior cavity will be found lined with dissected cubical crystals, fig. 12. *Sulphur* may be artificially crystallized by a similar process, and furnishes beautiful heaps of delicate prisms. The masses of crystallized *spermaceti*, often exhibited in shop windows, are obtained in the same way; and it is probable that the cavities in rocks and veins, bearing marks of igneous fusion, and often lined with magnificent specimens of crystalline minerals, owe their origin to some analogous process.



Crystallization of Bismuth.

There is another way of showing the crystalline texture of metals, which, with some of them, answers very well. It consists in washing over a thin plate of the metal with some acid which acts upon its surface. If tinfoil or tin-plate be thus washed over with dilute nitro-muriatic acid, the crystallization of the tin is often rendered beautifully manifest: this has been applied to ornamental purposes, under the name of *moirée metallique*, and different colours are easily given to the reflecting surface of the metal by the application of transparent varnishes.—(See TIN for more full details of this process). Mr. Daniell also developed the crystalline texture of several of the metals by steeping masses of them in acids, by which their surfaces were carved out like the alum in water: and the crystalline structure of a bar of tin was beautifully shown by placing it horizontally in mercury and turning it frequently upon its different faces so as to insure uniformity of action; in about twenty-four hours fissures appear along its lateral and terminal edges which, by gradually splitting, resolve the bar into four equal trihedral rectangular prisms, which, as well as two pyramids from their extremities, may be separated from each other by the point of a knife: it is indifferent to this result whether the square form be given to the bar by casting, hammering, or the filing down of any

other shape. Mr. Daniell further observes, in reference to this development of crystalline architecture, that "if a large crystal of sulphuret of antimony be introduced into a portion of fused sulphuret, and the heat be moderately continued, it will begin to melt down; but so far from this taking place uniformly at the surface, crystals will sometimes be left projecting half an inch from it; and in other places the cavities left by fused crystals will be so large and have such perfect surfaces that their angles may readily be ascertained. In order to observe these phenomena it is only necessary to remove the half-fused piece of sulphuret from its hot bath and allow it to cool."

When bodies are raised in vapour, and this is again condensed into the *solid* state, the process is generally called *sublimation*, and is not uncommonly resorted to to obtain such volatile matters in the form of crystals. The appearance of *camphor*, when thus slowly sublimed, is often extremely beautiful; so also that of *Benzoic acid*. *Iodine* is another body well calculated for the experiment: put a little of it into a clean Florence flask, and gently heat it; it will presently be converted into a deep violet vapour, which, subliming to the cold parts of the vessel, will there condense in small brilliant crystals of octoëdral and rhomboidal figures. There is a substance called *Naphthalin*, obtained during the distillation of coal-tar, and which may commonly be procured at gas-works: when pure, it is white and crystalline, and, if heated in a large phial or flask, its vapour congeals in lamellar crystals of extreme tenuity, crossing each other in all directions, and exhibiting a very singular appearance. *Calomel* and *corrosive sublimate* may be crystallized by a similar process, but the temperature required for their sublimation is considerable; and good crystals can only be obtained by operating upon large quantities, and subliming them very slowly. When flakes of *snow* are examined, they are found to be a congeries of crystals of ice produced by the cooling of the vapour of water.

Some substances are so easily decomposed by heat, and at the same time retain water with such avidity, that it is impossible to crystallize them by any of the above processes: in these cases, crystallization may sometimes be effected by placing the solution under the exhausted receiver of an air-pump, over a surface of sulphuric acid, which, by absorbing the vapour as it rises, causes rapid evaporation at a low temperature.

Some salts may be brought to crystallize by the addition of substances having a strong affinity for water, by which its attraction for the dissolved matters is weakened: thus alcohol, added to certain aqueous saline solutions, produces a separation of crystals, but they are generally small and indistinct.

When two salts of different solubilities are present in the same solution, they often may be separated by crystallization, that which is least soluble constituting the earlier crop of crystals. This method, however, is frequently ineffectual, especially with isomorphous salts, and with such as form triple combinations. When the *sulphates of iron* and *copper* are in solution together, crystals may be obtained of the same form as those of sulphate of iron, but containing variable proportions of sulphate of copper: in the same way the *sulphates of zinc* and *manganese*, and of

magnesia and *manganese*, crystallize together. In all these cases an atomic analogy prevails in the composition of the salts. The formation of *triple salts* is also a common occurrence: a familiar instance is afforded by the *tartrates of potassa and of soda*, the solutions of which, when mixed and evaporated, yield a crop of distinct triple crystals.

Crystallization is accelerated by introducing into the solution a *nucleus*, or solid body, upon which the process begins; and manufacturers often avail themselves of this circumstance. Thus we see *sugar-candy* crystallized upon strings, and *verdigris* upon sticks. There are cases in which it is particularly advantageous to put a few crystals of the dissolved salt into the solution, which soon cause a crop of fresh crystals. And if, for this purpose, we select very perfect forms, they will increase in size as the evaporation proceeds, and being daily turned, so that all sides may receive increments of solid matter in succession, they often produce large crystals of great perfection; but, in proceeding thus, care must be taken not to elevate the temperature of the solution, for if it be raised only a few degrees, portions of the newly-formed crystals are generally redissolved. "Dr. Wollaston made a remark upon the spontaneous growth of large crystals at the expense of small ones in the same solution, exposed to changes of temperature, which illustrates in a beautiful manner, the alternate ascendancy of the two antagonist forces. When the temperature rose the solvent power of the liquid was increased, and some of the solid matter of the crystals was abstracted; but when the temperature again fell this was deposited in a greater proportion upon the larger masses than upon the smaller, so that the latter were in the end entirely taken up and deposited upon the former."—(DANIELL, §. 106.) In some instances, if there be two salts in solution, that will most readily separate of which the crystals have been introduced. Thus, if we dissolve two parts of nitre and three of sulphate of soda in five of warm water, and fill two bottles with the solution, putting into one a crystal of nitre, and into the other a crystal of sulphate of soda, and placing both in ice-cold water, nitre only will crystallize in the one, and sulphate of soda in the other.

A strong saline solution, excluded from the *air*, will frequently crystallize the instant that air is admitted. For this purpose a strong solution of sulphate of soda (3 lbs. of the crystallized salt, to 2 lbs. of water) may be most conveniently used: it should be poured whilst hot into a flask, and tied over with bladder, or secured by a good cork: when cold it remains liquid, but on perforating the bladder, or withdrawing the cork, it gradually shoots from the surface downwards, into a fibrous mass of crystals. This phenomenon has been unsatisfactorily referred to atmospheric pressure. (GAY LUSSAC, *Ann. de Chim.*, vol. lxxxvii.) Mr. Graham (*Edinb. Phil. Trans.*, 1828,) ascribes it to the chemical union of air with the water holding the salt in solution. In other cases, agitation, or the dropping in of a crystal or other solid, produces the same effect. Such phenomena have been shown by Dr. Ure to be affected by electrical changes: he found that, in the voltaic circuit, crystallization always began at the negative pole; but as alkali is there elicited, it may have tended to accelerate the process; or the acid evolved at the positive pole may have retarded it. (*Quarterly Journal*, vol. x., p. 6.)

The presence of *light* also influences the process of crystallization. Thus we see the crystals collected in camphor-bottles in druggists' windows always most copious upon the surface exposed to light; and if we place a solution of nitre in a room which has the light admitted only through a small hole in the window shutter, crystals will form most abundantly upon the side of the basin exposed to the aperture through which the light enters, and often the whole mass of crystals will turn towards it. On looking over the preparations upon the shelves of the laboratory, we frequently meet with analogous cases of crops of crystals formed upon the sides of the bottles facing the windows.

Many saline solutions form arborescent crystalline pellicles, when left to spontaneous evaporation, which slowly travel up the sides of the basin, and gradually proceed down upon the outside; this process also often begins on the side nearest the light, and is sometimes confined to it. Acetate of lime exhibits this appearance in a very beautiful manner. (AIKIN'S *Dict.*, Art. LIGHT.) It is often the result of the capillary attraction of the crystals formed upon the edge of the solution.

The forms of crystals are frequently modified in a remarkable manner by the *medium* from which they are deposited, independent of any chemical change: thus in foul and muddy liquids the crystals are usually deposited in their simplest forms; in gelatinous and saccharine solutions crystals are generally single, and remarkably sharp and regular. Common salt deposited from an aqueous solution containing urea, crystallizes in octoëdra instead of cubes, which are its usual figure; and sal ammoniac under the same circumstances forms cubes, whereas in pure water its crystals are octoëdral. Berzelius says, that very large crystals of nitre may be obtained from its solution in boiling lime-water, which has no analogous effect upon other salts.

Some substances remarkably interfere with the appearance and forms of crystals, although contained in them in very minute quantities; this is especially the case with some of the *hydrocarbons*. If 1 part of the liquid obtained by the compression of oil-gas, and which always exists as vapour in it, be mixed with 8 or 10 parts of strong oil of vitriol, a dark liquor is produced; from this, when diluted with water, filtered, and converted by the addition of carbonate of potash into a sulphate of potash, a salt is obtained, which, upon crystallization, is nacreous, in the form of scales, and has nothing in its appearance common to sulphate of potash: it is however that salt; and is thus affected by the presence of a substance which sometimes does not amount to a two-hundredth part of the salt. The same substance has a still greater power over the sulphate of copper, and in increased quantities (still comparatively small), influences the appearances of other saline bodies.

Independent of the beautiful application of the process of crystallization in refined chemistry to determine the *nature* of bodies by the careful inspection of their forms, the manufacturer avails himself of it to cleanse, purify, and prepare a number of substances useful in the arts, the purity of which is often judged of by the regularity and perfection of their crystalline figures. Common salt is thus obtained by the evaporation of sea-water, and of brine-springs, in consequence of its tendency to crystallize in hot liquors, which retain the other salts that are present in

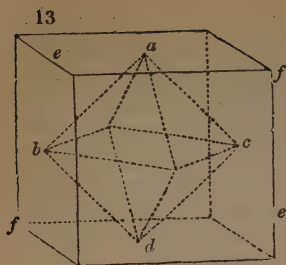
more permanent solution. Epsom salt, or sulphate of magnesia, is freed by crystallization, from the chloride of magnesium with which it is mixed in the residue of sea-water, after its common salt has been taken out: the magnesian chloride is very difficultly crystallizable, and remains in what is called the *mother liquor*, or residuary solution, which on account of its excessive bitter taste, is known in our salt-works by the name of *bittern*. Nitre is refined, by the facility of its crystallization, for the manufacture of gunpowder, and so cleansed of common salt and other impurities with which it is usually contaminated in the state in which it is imported from India. Numerous other instances of the application of the process of crystallization to the purposes of the arts and manufactures will appear in the sequel.

§ 2.—THEORIES OF CRYSTALLIZATION.

WE may now proceed to notice the *structure* of crystallized bodies, upon which the *Theories of Crystallization* are founded.

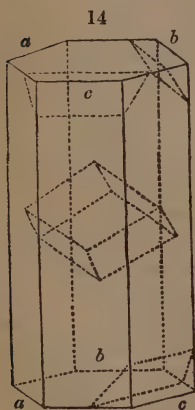
It has already been observed, that crystallized bodies, natural and artificial, affect one form in preference to others. The fluor-spar of Derbyshire crystallizes in cubes; so does common salt. Nitre assumes the form of a six-sided prism, and sulphate of magnesia that of a four-sided prism. But these forms, especially as respects natural crystals, are liable to various modifications. Fluor-spar sometimes crystallizes in the form of octoëdra; and there are so many forms of carbonate of lime that it is difficult to select that which most commonly occurs. Romé de L'isle referred these variations of form to certain truncations of an invariable primitive nucleus; and Gahn afterwards observed, that when a piece of calcareous spar was carefully broken, all its particles were of a rhomboidal figure. This induced Bergman to suspect the existence of a primitive nucleus in all crystallized bodies (*Physical and Chemical Essays*, vol. ii., p. 1). When Haiüy entered this field of inquiry, he not only corroborated the opinions of Bergman, and submitted former hypotheses to experimental proof, but traced with much success the laws of crystallization, and pointed out the modes of transition from primary to secondary figures. (*Traité de Minéralogie*, Paris, 1801.) Since the time of Haiüy the study of crystallization, especially in its relations to mineralogy, has been pursued and extended by G. Rose, (*Elements of Crystallography*,) by Professor Whewell, (*Philosophical Transactions*, 1825,) by M. Mohs, and by Professor Weiss, of Berlin; the latter is the founder of a new system of crystallography, having reference to the geometrical relations of their exterior forms rather than to their ultimate molecules or internal structure.

Those who are in the habit of cutting and polishing certain gems, have long known that they only afford smooth surfaces when broken in one direction; and that in others the fracture is irregular and uneven. This is the case with crystallized bodies in general. If we attempt to split a cube of fluor-spar with the blade of a knife, assisted by a hammer, we shall find that it will only yield kindly in the direction of the solid angles; and pursuing the division in these directions, an octoëdron will be the resulting figure, as in fig. 13. The new planes resulting from this *cleavage* of the crystal, are called its *cleavage-planes*. The line



produced by the meeting of two planes is the *edge* of the crystal: and the meeting of any two lines or edges, forms a *plane angle*. A *solid angle* is produced by the meeting of three or more plane angles. In the annexed diagram, $abcd$ are the exterior planes of the crystal; ee its edges; ff its solid angles. (For further details respecting these terms, see Mr. BROOKE'S *Familiar Introduction to Crystallography*.)

In splitting a six-sided crystal of calcareous spar, we find that of the six edges of the superior base three alternate edges only will yield to the blow: those, for instance, marked a, b, c , (fig. 14); and the division will take place in a plane inclined at an angle of 45° . The three intermediate edges resist this division. But in dissecting the inferior base of the crystal, the intermediate edges will alone yield, namely, a, b, c . If we continue this dissection in the same directions, we shall at length obtain the obtuse rhomboid, which is seen in this diagram in its relative situation to the including prism.

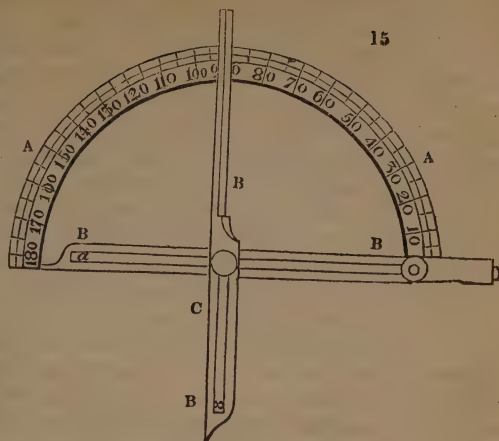


We thus then arrive at the *primitive form* of the calcareous spar; and from whatever secondary form it has been obtained, it is always a *rhomboid*, having obtuse angles of $105^\circ 5'$. But an obtuse rhomboid is also the primitive form of other bodies, as of pearl-spar, iron-spar, and tourmalin. But here the inclination of the surface points out a difference. Thus the primitive angle of pearl-spar is $106^\circ 5'$, of iron-spar 107° , (Wollaston, *Phil. Trans.*, 1812,) and of tourmalin $113^\circ 10'$. The temperature, however, at which these measurements are taken, should be noted, for it appears to affect the mutual inclinations of the planes of crystals. In the case of carbonate of lime, it amounts, according to Mitscherlich (*Ann. de Ch. et Ph.*, xxv. 108), to as much as $8\frac{1}{5}$, in the interval of temperature between 32° and 212° . As

the temperature augments, the obtuse dihedral angles diminish; that is, the smaller axis of the rhomboid dilates more than its other diagonals, so as to cause an approach to the cubical form. When melted litharge is allowed slowly to solidify and cool, when it reaches a particular temperature it splits into small fragments: if a little of the double sulphate of potassa and copper be fused over a spirit lamp, it congeals into a brilliant green solid; but as its temperature falls to about 212° , it suddenly is resolved into a heap of incoherent powder. These phenomena are referred by Mr. Daniell to the inequality of their respective contractions.

The instruments which are used for measuring the angles of crystals are termed *goniometers*. The simplest of these (fig. 15) consists of a protractor, or semicircular scale of degrees, AA , and a small pair of compasses or nippers, BBB , destined to receive the crystal.

The centre of the pair of compasses is made moveable, like those of the common proportional compasses, so as to permit the legs BB, and BCB to be considerably lengthened or shortened, when the two pieces are applied to each other. The fixed leg, BB, is represented as beneath the moveable one BCB, or radius measuring 90° , and the lower end of the centre-pin, which could not be shown in

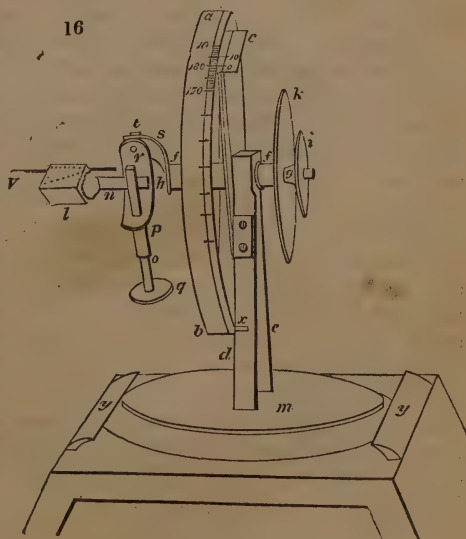


the wood-cut, is made to fit the hole or centre in the protractor precisely at the same time that a stud or projecting piece of brass, being admitted into the long perforation *a* of the leg BB, the piece becomes steadily attached to the protractor or semicircle, as is seen in the figure.

The application of this instrument is obvious. The crystal to be measured is applied between the compasses, which, being thus set, are applied to the protractor, and the value of the angle may be read off at the fiducial edge of the leg BCB. It is, however, seldom that accurate results can thus be attained, for the surfaces of crystals are generally too small or too imperfect, to admit of such method of measurement.

The *reflective goniometer* (fig. 16), invented by Dr. Wollaston (*Phil. Trans.* 1809), is a more useful and perfect instrument. It enables us to determine the angles even of minute crystals with great accuracy; a ray of light reflected from the surface of the crystal being employed as radius, instead of the surface itself. Mr. W. Phillips has given the following description and practical details for the use of this instrument, in his *Introduction to Mineralogy*.

a b is the principal circle, graduated on one edge to half degrees, and divided, for convenience into two parts of 180° each; (it is graduated only in part in



the annexed sketch). c is a brass plate, screwed upon, and supported by, the pillar d , and graduated as a vernier. ff is the axle of the circle ab , and passes through the upper part of the two pillars de , the other ends of which are inserted into a wooden base m . gh is an axle, enclosed within ff , and turned by means of the smallest circle i , which communicates a motion to all the apparatus on the left of h , without moving the principal circle ab . k is a circle, to which is attached the axle of the principal circle. If therefore we would move the latter, it will be done by moving k , and as the axle of the principle circle includes that of the apparatus on the left of h , we must necessarily give a motion to the whole instrument by moving the circle k .

These two movements being understood, let us now suppose that we want to measure a crystal; a rhomboid of carbonate of lime, for instance*. Let l be the rhomboid, attached by means of wax to one end of a plate of brass n ; the other end of the plate being placed in a slit in the upper part of the circular brass stem o , which passes through the tube p , to which it is so adjusted as to allow of being moved either up or down, or circularly, by means of the circle q . The tube p is fixed to the curved brass plate r , which is attached, but so as to allow of motion, to another curved plate s , by means of a pin t , the other end of the latter plate being connected with the concealed axle gh , to which a motion is given by turning the little circle i . By means of the pin t and the tube p , therefore, we have two motions, in addition to the two before described as belonging to the axles of the instrument. The inner axle, however, may be said to be the centre of all the motions. It will, therefore, be of advantage that the rhomboid of carbonate of lime should be placed as nearly on a line with that axle as possible: this will be sufficiently adjusted by means of the stem o , which admits of being raised or depressed at pleasure.

The use of this instrument depends on the reflecting power of the polish on the natural planes, or fractured surfaces of minerals: and that this is in some cases very powerful, any one may convince himself by looking upon a very brilliant plane, held beneath the eye, with its edge nearly touching the lower lid, and not far distant from a window; he will then observe the reflection of the bars very distinctly. Let us then suppose the goniometer, as above represented, to be distant from a window from eight to twenty feet. Let, then, v be a *black line* (the use of this is essential) drawn on the wainscot between the window and the floor, and *perfectly parallel* with the horizontal bars of the window. If, then, the eye be placed almost close to the rhomboid l , a reflection of one of the bars will be seen on one of its planes. Let us suppose the reflection to be in the direction of the lower dotted line on the plane; and it will be clear that it cannot be parallel with the bar of the window, not being even with the black line v . It must therefore be adjusted.

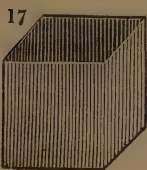
* As it is necessary that this instrument when used should be perfectly steady, it should be placed upon a firm table, and may be raised to a convenient level (about a foot above it), by its

pyramidal case, the top of which is represented in the wood-cut; m is the base of the goniometer, and $y y$, two hollowed slips of wood which receive it.

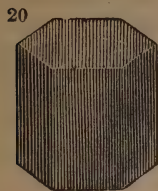
This may, perhaps, be done by slightly drawing to the left the circle g , which communicates motion by means of the pin t ; or perhaps it may be done by giving a circular motion to the stem o . By one of these two motions, or by both, it may certainly be effected. If, however, the reflection appears to be like the upper dotted line, that is, parallel with the black line, v , we must first convince ourselves that it is so, simply by depressing the crystal a little by means of moving the little circle i , so as to bring the reflection *upon the black line*. This being adjusted, which must be done precisely, we then turn the crystal, by turning the little circle i , until the reflection of the *same bar* be seen on the next plane, perfectly *on a line with and upon the black line v* . However, in adjusting the second, we may disturb the first reflection. By perseverance it will be found that both can be adjusted by means of one or other of the movements by the stem o , or the pin t , or by the help of both, and a short experience will do away the chief difficulties. Both reflections being precise, we are now, by means of the circle k , to turn the principal circle until it is arrested by the stop x on the pillar d ; it will then be found that 180 on the principal circle coincides with o on the vernier. In doing this, however, we may slightly disarrange the reflections on the plane of the crystal, which may be re-adjusted simply by moving the little circle i , which will not disturb the principal circle $a b$: we must be certain, however, *that 180 on it forms a line with o on the vernier, at the same time that the reflection of the bar is seen along the black line*. One movement more, and the measurement will have been made. Turn the circle k , keeping the eye almost close to the rhomboid, until the reflection of the *same bar* is seen on the adjoining plane *precisely upon the black line v* , and the operation is completed. It must then be observed what proportion of the principal circle has been moved. Suppose that 105 on it be now on a line with o on the vernier;—it is the value of the angle. But suppose it to be a little more than 105 and less than $105\frac{1}{2}$: it must then be observed *which line of the vernier touches, or forms but one line with*, another line on the principal circle: suppose it to be 5 on the vernier, the angle is then $105^{\circ} 5'$, which is the true value of the obtuse angle of a rhomboid of carbonate of lime.

In following the method of dissection above described, Haüy obtained six *primitive forms*, which by further mechanical division, may be reduced to three *integral elements*. The primitive forms are:—

1. The cube parallel-opipedon, &c. (Fig. 17.)
2. The tetraëdron. (Fig. 18.)
3. The octoëdron. (Fig. 19.)



4. The hexangular prism. (Fig. 20.)



5. The rhombic dodecaëdron. (Fig. 21.)

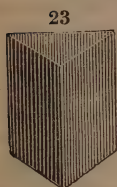


6. The dodecaëdron with isosceles triangular faces. (Fig. 22.)



The integral elements are:—

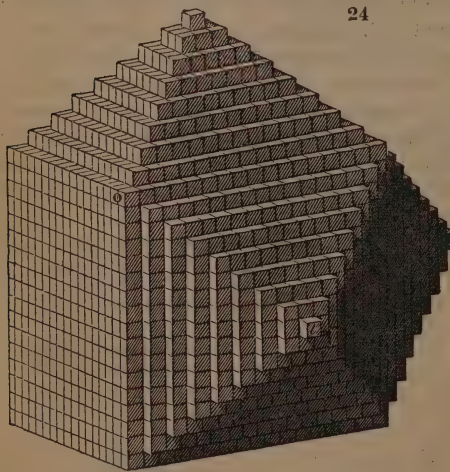
1. The parallelopiped, or simplest solid, having six surfaces parallel two and two. (Fig. 17.)



2. The triangular, or simplest prism, bounded by five surfaces. (Fig. 23.)

3. The tetraëdron, or simplest pyramid, bounded by four surfaces. (Fig. 18.)

The *secondary* forms are supposed to arise from *decrements* of particles taking place on different edges and angles of the primitive forms. Thus a cube, having a series of decreasing layers of cubic particles upon each of its six faces, will become a dodecaëdron, if the decrement be upon the edges (fig. 24); but an octoëdron, if upon the angles; and by irregular, intermediate, and mixed



decrements, (fig. 25), an infinite variety of secondary forms would ensue, as the annexed figures show. It thus appears then, that every crystal may be supposed to include an invariable nucleus, or *primary* form, from which the *secondary* forms are derived, by certain *laws* of *decrement*.

The above illustrations have been taken from Haiiy as furnishing the simplest instances of these theoretical views, but other crystallographers have given very different statements of the number and nature of the primary

forms. Mr. Brooke (*Introduction*, p. 6) has enumerated fifteen, namely, 1. The *cube*, contained within six square planes (fig. 17). 2. The *regular tetraëdron*, contained within four equilateral triangular planes (fig. 18). 3. The *regular octoëdron*, resembling two four-sided pyramids united base to base; the planes are equilateral triangles, and the common base of the two pyramids (or the *base* of the *octoëdron*) is a square (fig. 19).

4. The *rhombic dodecaëdron* contained between twelve equal rhombic planes (fig. 21).

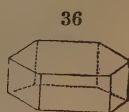
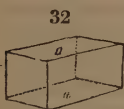
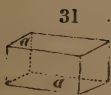
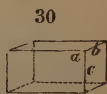
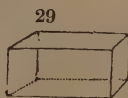
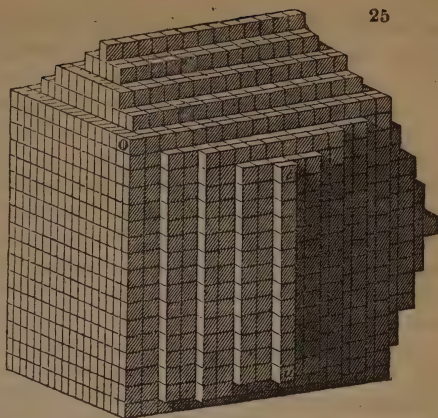
5. The *octoedron with a square base* (fig. 26), contained within eight equal isosceles triangular planes; the square base distinguishes it from figures 27 and 28, and is the only part of the figure which is constant.

6. The *octoëdron with a rectangular base*, its planes are generally isosceles triangles, but not equal (fig. 27).

7. The *octoëdron with a rhombic base*, contained

within eight equal *scalene* triangular planes: all its dimensions are variable (fig. 28). 8. The *right square prism* (fig. 29). (A prism is a solid whose lateral edges are parallel, and whose terminal planes are also parallel: those which stand perpendicularly when resting on their base, are called *right* prisms; those which incline, are called *oblique* prisms.)

9. The *right rectangular prism* (fig. 30), whose three edges, a b c , are unequal; for if any two of those were equal, the prism would be square.

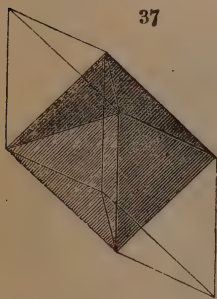


10. The *right rhombic prism* (fig. 31), differing from the preceding in the planes a a being rhombs. 11. The *right rhomboidal prism* (fig. 32), in which the planes a a are rhomboids. 12. The *oblique rhombic prism* (fig. 33). 13. The *oblique rhomboidal prism* or *doubly oblique prism* (fig. 34). 14. The *rhomboid*, or *rhomboëdron*, bounded by six equal rhombic planes (fig. 35). 15. The *regular hexagonal prism* (fig. 36). In reference to the geometrical relations of these forms to each other, and to the production of secondary forms, I must again refer to Mr. Brooke's *Introduction*.

The geometrical forms of crystals have been referred by Weiss to certain lines, in respect to which each face is accompanied by others having the same positions and properties, and which are termed *axes of symmetry*. A rhomboid of calc-spar, for instance, may be so placed with one

of its obtuse angles uppermost, as that the three faces which meet there shall be equally inclined to the perpendicular line. "In this position every derivative face which is obtained by any modification of the faces or edges of the rhomboëdron, implies either three or six such derivative faces; for no one of the three upper faces of the rhomboëdron has any character or property different from the other two; and therefore there is no reason for the existence of a derivative from one of the primitive faces which does not equally hold for the others. Hence the derivative forms will in all cases contain none but faces connected by this kind of correspondence; the axis thus made vertical will be an axis of symmetry, and the crystal will consist of three divisions ranged round this axis and exactly resembling each other. But this is only one of the kinds of symmetry which crystalline forms may assume: instead of being *uniaval*, they may have three axes of complete equal symmetry at right angles to each other, as the cube and regular octoëdron; or two axes of equal symmetry perpendicular to each other, and to a third axis which is not affected with the same symmetry with which they are; such a figure is a square pyramid: or they may have three rectangular axes all of unequal symmetry, the modifications referring to each axis separately from the other two. These systems are respectively distinguished in the nomenclature of Mohs as the *rhomboëdral*, the *tessular*, the *pyramidal*, and the *prismatic*." (DANIELL'S *Introd.* § 124. See also in reference to Weiss's system, TURNER'S *Elements of Chemistry*, 6th edit.)

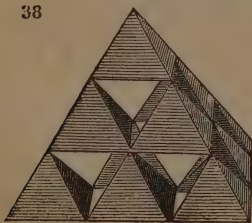
In examining the forms and texture of crystals, we occasionally



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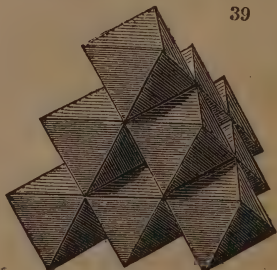
meet with cases to which the theories of primary and secondary forms are not satisfactorily applicable. A slice of fluor-spar, for instance, obtained by making two successive and parallel sections, may be divided into acute rhomboids; but these are not the primitive form of the spar, because, by the removal of a tetraëdron from each extremity of the rhomboid, an octoëdron is obtained (fig. 37). Thus, as the whole mass of fluor may be divided into tetraëdra and octoëdra, it becomes a question which of these forms is to be called primitive, especially as neither of them

can fill space without leaving vacuities, nor can they produce any arrangement sufficiently stable to form the basis of a permanent crystal. Mr. Daniell, in the following figures, has represented



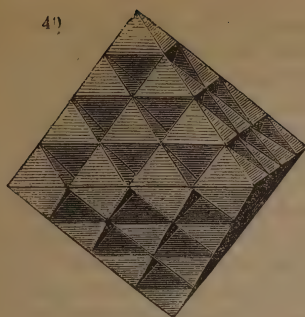
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Tetraëdral Tetraëdron.

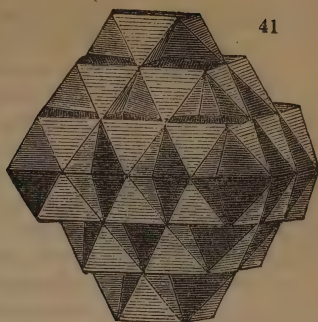


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Octoëdral Tetraëdron.



Octoëdral Octoëdron.

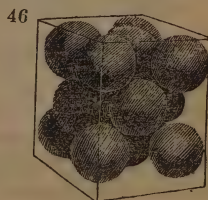


Tetraëdral Octoëdron.

these constructions of the tetraëdron and octoëdron each with tetraëdral and octoëdral particles, in which it is seen that the tetraëdral structure is interspersed with octoëdral vacuities, and the octoëdral with tetraëdral spaces; so that one might be conceived to be taken out of the other.

"All bodies," he observes, "may be considered as attracting each other, as if the whole of their matter were condensed into their centres of gravity, which therefore would in all cases be drawn as closely as possible together: under this law solid tetraëdra and octoëdra would apply themselves to each other by their sides, and not by their edges."

To obviate such incongruities, Dr. Wollaston (*Phil. Trans.*, 1813,) following out an hypothesis previously developed to a considerable extent by Dr. Hooke, proposed to consider the primitive particles as *spheres*, which, by mutual attraction, have assumed that arrangement which brings them as near as possible to each other. When a number of similar balls are pressed together in the same plane, they form equilateral triangles with each other (fig. 42); and if balls so placed were cemented together and afterwards broken asunder, the straight lines in which they would be disposed to separate would form angles of 60° with each other. A single ball, placed anywhere on this stratum, would touch three of the lower balls, and the planes touching their surfaces would then include a regular tetraëdron (fig. 43). A square of four balls, with a single ball



resting upon the centre of each surface would form an octoëdron (fig. 44); and upon applying two other balls at opposite sides of this octoëdron, the group will represent the acute rhomboëdron (fig. 45); or by placing a ball on each face of the octoëdron, it becomes a cube (fig. 46).

Thus the difficulty of the primitive form of fluor, above alluded to, is done away, by assuming a sphere as the ultimate molecule. By oblate and oblong spheroids other forms may be obtained. Thus by



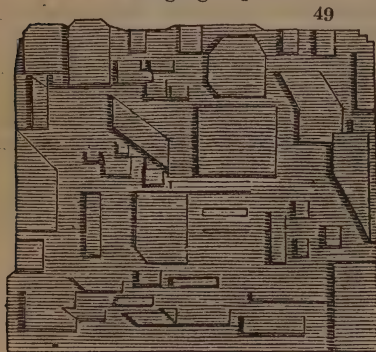
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oblate spheroids having their axes in the proportion of 1 to 2·87, an oblate rhomboëdron, the angles of which would correspond with those of calc-spar, would result, and all such solids would split in directions parallel to their faces (fig. 47). With *oblong* spheroids, on the contrary, (fig. 48), the centres would approach nearest to each other by mutual attraction when

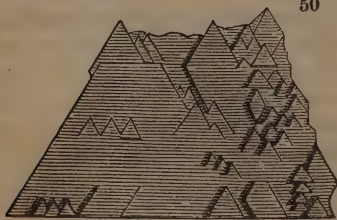


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their axes were parallel and their shortest diameters in the same plane; whence a solid which would split into plates at right angles to its axis, and the plates would be divisible into equiangular three or six-sided prisms; a cleavage belonging to phosphate of lime, to the beryl, and other minerals.



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Mr. Daniell (*Quarterly Journal of Science and the Arts*, vol. i., and *Journal of the Royal Institution*, vol. ii.) has offered some curious and important confirmations of Dr. Wollaston's hypothesis. If an amorphous piece of alum be immersed in water, and left quietly to dissolve, it is unequally acted upon by the fluid (see fig. 1): and the mass presents the forms of octoëdra, and sections of octoëdra, as it were carved or stamped upon its surface, as in the annexed figures, 49 and 50. This appearance is produced when the attraction of the water for the solid is nearly counterbalanced by its mechanical texture. The crystals formed by this species of dissection are highly curious, from their modifications and relative positions,

as the same group presents the primitive form, as well as its truncations and decrements.

Other salts yield other figures, and by more complicated chemical action, as of acids upon carbonate of lime, the metals, &c., analogous results are obtained. Here, then, instead of dividing a crystal by mechanical force, its structure is gradually developed by the process of solution. In these cases two circumstances are particularly remarkable; the crystals are different; and their forms vary with the different faces of the original mass. In one direction we observe octoëdra and sections of octoëdra; in another, parallelograms, modified by certain determinate intersections. If, in either of these positions, we turn the mass upon its axis, the same figures

are perceived at every quadrant of a circle; and if we suppose the planes continued, they will mutually intersect each other, and various geometrical solids will be constructed. In this way, alum alone furnishes octoëdrons, tetraëdrons, cubes, four and eight sided prisms, either with plain or pyramidal terminations, and rhombic parallelopipedons. It is evident, then, that no theory of crystallization can be admitted, which is not founded upon such a disposition of constituent particles, as may furnish all these modifications, by mere abstraction of certain individuals from the congeries, without altering the original relative position of those which remain; and these conditions may be fulfilled by such an arrangement of spherical particles, as would arise from the combination of an indefinite number of balls endued with mutual attraction; and no other geometrical solid is adequate to the purpose; and where bodies afford crystals differing from the octoëdral series, an analogous explanation is furnished by supposing their constituent particles to consist of oblate spheroids whose axes bear different proportions to each other in different substances. Hence we may also conclude, that the internal structure of all crystals of the same body is alike, however the external shapes differ. In corroboration of the above hypothesis, Mr. Daniell remarks that the hexaëdron is, of all geometrical figures, that which includes the greatest capacity under the least surface. "If, therefore, the ultimate particles of crystalline bodies be spheres or spheroids, the greatest possible number in the least space will be included in this form. It is probable that the exterior shape of every crystal is determined by the nucleus first formed by a certain definite number of particles, which, by the power of mutual attraction, overcome the resistance of the medium in which they were suspended, or from which they were separated. This number may vary with the solvent, or other contingent circumstances. Four spherical particles, thus united, would balance each other in a tetraëdral group, six in an octoëdral group, and each would present particular points of attraction to which all subsequent deposits would be directed. Now, let us imagine two nuclei formed in the same solution, whose axes run in contrary directions; their increase will consequently be in contrary directions, and each will attract a particular system of particles from the surrounding medium. If these two systems should cross each other in their course, a greater number will be brought within the sphere of mutual re-action at the point of junction, and they ought to arrange themselves in the least possible compass. The facts here answer to the theory. If we select any crystals, having others crossing them nearly at right angles, and separate them, the points of junction invariably present an hexaëdral arrangement."

We have already adverted to the important applications of the phenomena and process of crystallization to theoretical and practical chemistry. To the mineralogist, the science of crystallography is equally indispensable; it enables him to determine the species to which minerals belong, and to recognise their varieties by their external and mechanical characters.

Under the term *isomorphism* we have above alluded to the close approximation, if not identity, of form, which certain crystallized compounds of analogous atomic constitution assume. Of these isomorphous

bodies a table has been drawn up by Professor Johnston (*Report on Chemistry to the British Association*). The following are their principal groups, (TURNER'S *Elements*, 6th edit., p. 646,) their atomic analogies will be afterwards noticed.

1.	Silver.	8.	Salts of soda.
	Gold.		— oxide of silver.
2.	Arsenious acid.	9.	Salts of baryta.
	Sesquioxide of antimony.		— strontia.
3.	Alumina.		— lime (in aragonite.)
	Peroxide of iron.		— oxide of lead.
4.	Arseniates.	10.	Salts of lime.
	Phosphates.		— magnesia.
5.	Sulphates.		— protoxide of iron.
	Seleniates.		— manganese.
	Chromates.		— zinc.
	Manganates.		— nickel.
6.	Perchlorates.		— copper.
	Permanganates.	11.	Salts of alumina.
7.	Salts of potassa.		— peroxide of iron.
	Salts of ammonia, with 1 atom of water.		— oxide of chromium.
			— sesquioxide of manganese.

Dr. Turner observes that there are other analogies among isomorphous bodies independent of form: arsenic and phosphorus for instance resemble each other in odour, in forming gaseous compounds with hydrogen, in the relative proportions of oxygen with which they combine, and in the quantity of water in their salts. Selenium and sulphur resemble each other in fusibility, volatility, and combustibility, and in forming analogous atomic compounds with hydrogen and with oxygen: sulphuric acid and selenic acid, and their respective salts, are equally allied. Baryta and strontia, lime and magnesia, cobalt and nickel, exhibit similar relationships. Isomorphous substances also readily crystallize together, and are difficultly separated. Dr. Daubeny, for instance, found that a weak solution of lime in water is very sluggishly affected by the delicate test of oxalate of ammonia, when much sulphate of magnesia is at the same time present; and Dr. Turner found that chloride of magnesium could not be purified from lime by oxalate of ammonia. From a mixed solution of the protosulphates of copper and iron, crystals, retaining the same quantity of water, and having the same form as those of protosulphate of iron, are obtained, though they include a large quantity of copper. The protosulphates of zinc and copper, of copper and magnesia, of copper and nickel, zinc and manganese, manganese and magnesia, crystallize together, having the same form and the same quantity of water as the protosulphate of iron. These salts are not separable by repeated crystallizations, and yet they are not chemically united in definite proportions as true double salts, but merely crystallize together. In minerals similar isomorphous mixtures occur: thus the garnet is a double silicate of alumina

and lime, in which, as also in alum, the alumina may be replaced by peroxide of iron; or they may be both present in any proportion, provided their sum be equivalent to either singly. So also while peroxide of iron replaces the alumina, the lime might be replaced by protoxide of iron, and a mineral would result, having the form of the garnet, but containing neither alumina nor lime, and being in fact a compound of the silicate of peroxide of iron with the silicate of protoxide of iron, instead of, as in the garnet, silicate of alumina with silicate of lime. Other substitutions of isomorphous elements or compounds might take place without influencing the crystallographic character; and from other mineral compounds similar instances might be selected.

Another curious fact in regard to crystals, also noticed by Mitscherlich, is the assumption by the same substance of two incompatible crystalline forms: such bodies are therefore called *Dimorphous*. This is the case with sulphur, which when crystallized by fusion yields oblique rhombic prisms, but is deposited from certain of its solutions in rhombic octoëdrons. Pure carbon, in the form of diamond, crystallizes in octoëdrons, but as graphite, in hexagonal plates. Carbonate of lime in calc-spar has the rhomboëdral structure, but in arragonite that of the rectangular octoëdron; and there are other analogous cases. It has been found in regard to these cases of dimorphism that each form has its peculiar density; the specific gravity of calc-spar for instance being 2.71; that of arragonite is 2.94. The temperature too at which the crystals are formed is another influencing cause: thus when carbonate of lime is precipitated by adding chloride of calcium to carbonate of ammonia, the grains of the powder are rhomboëdral if thrown down at the temperature of 50° , but octoëdral, if at 150° . (G. ROSE, *Phil. Mag.*, xii., 465.)

There are, moreover, some cases in which solids themselves change their molecular arrangement: thus sugar which has been boiled down to such a consistency as to solidify on cooling, forms a transparent vitreous mass, as seen in what is termed *barley-sugar*; but this, if kept for some time, becomes opaque, granular, and friable. Old brass wire is apt to grow brittle. Prismatic crystals of sulphate of nickel and of seleniate of zinc, when exposed to the sun, become opaque, and break up into small octoëdrons. Crystals of sulphate of magnesia or of sulphate of zinc, heated in oil to a temperature of about 126° , become opaque, and when broken are found to consist of a number of individual crystals, easily separated. (MITSCHERLICH. See also METHUON, *Quart. Journ.* i., p. 123, and GREGORY WATT's experiments on the effect of slow cooling upon certain substances, *Phil. Trans.* 1804, p. 279.) Dr. Macculloch has noticed the crystalline texture occasionally acquired by some kinds of sandstone, which, having served for the hearths of furnaces, have been long exposed to heat, though always far below their point of fusion. But no modification of form is more remarkable than that of *glass*, a state, of which many bodies are susceptible, and characterized by a curved or conchoidal (*glassy*) fracture; it never breaks with plane surfaces or *sparry*. Under certain circumstances, however, vitreous compounds pass into crystalline forms, and in large masses of glassy slag, globular nodules of radiating and acicular crystals are not very uncommon. Arsenious acid presents a similar phenomenon: when recently fused or sublimed it is usually

glassy and transparent, but it gradually becomes an opaque, white, crystalline solid; the change commencing at the surface, and gradually proceeding to the centre. This change from the vitreous to the crystalline state sometimes takes place suddenly, and gives rise to a curious phenomenon observed by G. Rose: the vitreous acid, when dissolved in hot and dilute hydrochloric acid, deposits crystals of the opaque acid, and a flash of light is emitted at the formation of each crystal; this appearance is not observed when the hydrochloric solution is made with the opaque or crystalline, instead of the transparent or glassy, acid.

There are other cases in which what may be termed dimorphism is to a certain extent produced by changes of temperature. Thus the red sulphuret and the red oxide of mercury both become black when highly heated, but reassume their red colour on cooling; periodide of mercury is often yellow whilst hot, but becomes scarlet as it cools. Oxide of zinc is yellow whilst hot, and white when cold. Even gaseous bodies are susceptible of changes of this kind, of which nitrous acid vapour furnishes an instance, being nearly colourless when very cold, but of a deep orange when heated. When precipitated sulphuret of antimony is dried at about 400° it retains its deep orange colour, but when heated a little higher, it shrinks, blackens, and acquires a metallic lustre, without further loss of weight; and on the other hand, the black sulphuret, when strongly heated, and suddenly cooled by throwing it into water, acquires a brown colour.

Certain metallic oxides, such as alumina, peroxide of tin, and oxide of chromium, become insoluble in acids after having been heated to redness; and some of them, in passing from the soluble to the insoluble state, suddenly become luminous, and rise greatly in temperature: this is remarkably the case with gadolinite, which glows when heated, and changes colour, but sustains no change of weight.

The cause of many of these extraordinary phenomena, in which bodies undergo changes in form and properties, whilst their composition is not apparently altered, may in some instances no doubt be referred to modifications of their molecular arrangements; in other cases the loss or evolution of heat is apparent. "The circumstance," says Professor Graham (*Elements of Chemistry*, part ii.), "most certain respecting this change in bodies is that they do not contain a quantity of heat after the change, which they must have possessed before its occurrence, in a combined or latent form. No ponderable constituent is lost, but there is this loss of heat. A change of the arrangement of the particles, it is true, might occur at the same time in some of these bodies, such as is observed when sulphite of soda is converted by heat into a mixture of sulphate of soda and sulphuret of sodium, without change of weight; but it would be difficult to apply an explanation of this nature to oxides, such as alumina and peroxide of tin, which contain only two constituents. The loss of heat observed will afford all the explanation necessary, if heat be admitted as a constituent of bodies equally essential as their ponderable elements. As the oxide of chromium possesses more combined heat when in the soluble than in the insoluble state, the first may be justly viewed as the higher *caloruret*, and the body in question may have different proportions of this as well as of any other constituent."

CHAPTER II.

HEAT, LIGHT, AND RADIANT MATTER.

HEAT—ITS EFFECTS AND SOURCES.

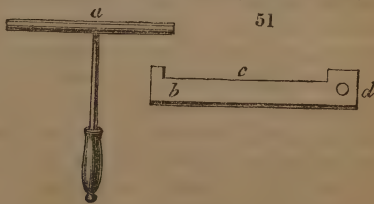
HEAT may be considered as the antagonist power to attraction*, one of its most obvious effects being the dilatation or expansion of bodies; so that, whenever a body is heated, it is enlarged in bulk, and consequently diminished in specific gravity. These changes are temporary only; for, on cooling, the body regains its former dimensions, and a further reduction of heat causes a proportionate diminution of bulk: hence, bodies are said to *expand when heated*, and to *contract when cooled*; a law to which the exceptions are very limited.

We know nothing of the *cause* of heat, but we generally refer the effects perceived to the presence of a highly attenuated and imponderable fluid, the particles of which repel each other, but are attracted by all other substances: it is supposed to pervade all matter, and to be diffused over the whole universe. To this supposed subtle fluid the French nomenclaturists gave the name of *caloric*—a term which has been much employed, under the idea that the word *heat*, which is applied both to cause and effect, might lead to ambiguity: this, however, it need not; and whatever may be the cause of the phenomena, *the word heat may be used to denote that state or condition of a body which excites in us the sensation of heat.*

§ 1.—EXPANSION IN GENERAL.

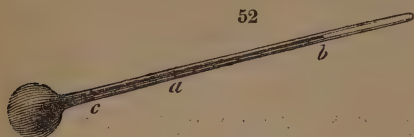
BODIES exist in nature under three forms,—*solids, liquids, and gases or vapours*; these three forms of matter suffer expansion and contraction in very different degrees, when exposed to similar changes of temperature: in solids, the change of dimensions is comparatively small, and refined means are necessary to determine and measure it; in liquids it is more obvious; and in gases extremely apparent.

To show the *expansion of a solid*, a bar of metal for instance, we may be provided with a gauge which measures its length and breadth at ordinary temperatures; and it will be found that, when heated, it will no longer pass through the apertures which readily admitted it when cold. *a* (fig. 51) is a brass bar with a handle attached, the length of which, at common temperatures, is exactly equal to the notch *c* in the plate *b*, and it exactly passes into the circular aperture *d*. If the bar be now heated by plunging it into boiling water, it will be found so much enlarged in all its dimensions, as not to pass through the apertures. If, on the contrary, it be cooled by ice, it will then contract, and pass them more readily.



* Fresnel observes that a sensible repulsive power is conferred by heat upon bodies delicately suspended in vacuo.—(*Ann. de Ch. et Ph.*, xxix., 57 and 107.)

The expansion and contraction of a *liquid*, when heated, are easily shown as follows: pour into a large thermometer tube (fig. 52) a quantity of brandy, so as to fill the bulb, and rise in the stem up to the mark *a*. Plunge it into warm water, and the spirit will dilate and rise in the tube up to the point *b*; remove it, and suffer it to regain its original temperature, and its bulk will return to *a*; but if it now be put into ice, the liquid will contract, falling in the tube to *c*; but again expanding, when removed into the atmosphere at ordinary temperatures.



Aëriform bodies far exceed the former in expansibility. Place a thermometer-tube, with its open end in a glass of water, as in fig. 53, and apply the heat of the hand to the bulb *a*; this will be sufficient to expand the air within, so that bubbles will escape through the water, and on removing the source of heat, the water will mount in the tube, showing, by the place it occupies, the degree of expansion which the air had suffered.

Thus far the general fact of the *expansion of the different forms of matter by heat, and their contraction by cold*, is easily demonstrated; but there are peculiarities belonging to each, and applications resulting from them, which must be entered into more in detail.

§ 2.—OF THE EXPANSION OF SOLIDS.

DIFFERENT solids possess different degrees of expansibility, and among them the *metals* are most susceptible of change of bulk; but each solid possesses a rate of expansion of its own. Lead, for instance, expands in volume one-350th; iron, one-800th; glass, one-1000th; in other words, 350 cubic inches of lead become 351; 800 of iron, 801; and 1000 of glass, 1001. In consequence of the numerous purposes to which glass and the metals are applied, and with which these changes of bulk interfere, it becomes necessary to examine their extent with precision.

The following table shows the linear dilatation of glass and several of the metals between the freezing and the boiling point of water. (DANIELL.)

1000000 of Glass tube . become	1000861	1000000 of Copper . become	1001712
" Crown glass "	1000875	" Brass "	1001783
" Platinum "	1000856	" Silver "	1001890
" Cast iron "	1001111	" Tin "	1001937
" Steel "	1001189	" Lead "	1002867
" Gold "	1001460		

The expansion in volume may be obtained without sensible error by trebling the number which expresses the increase in length, where, as in the above cases, the fraction of its length is small; thus, if a glass tube elongates by one-1248th when heated from 32° to 212° , its cubic space will have increased by three-1248ths; or one-416th of its former capacity.

In the range of temperature between 32° and 212° , these expansions are apparently nearly equable; but the experiments of Dulong and Petit (*Ann. de Chim. et Phys.*, and *Annals of Philosophy*, xiii. 164), prove that the rate of expansion increases with the temperature, as shown in the following tables:—

I. Increasing Dilatation of Glass by Heat.

Temperature by Air Thermometer. (Fahrenheit.)	Mean absolute Dilatation of Glass for each Degree.	Temperature by a Thermometer made of Glass.
From 32° to 212°	$\frac{1}{69660}$	$212^{\circ}0$
„ 32° to 392°	$\frac{1}{65340}$	$415^{\circ}8$
„ 32° to 572°	$\frac{1}{59220}$	$667^{\circ}2$

II. Increasing Dilatation of Metals by Heat.

Temperature by Air Thermometer.	Mean Dilatation of Iron for each Degree.	Temperature by Iron-rod Thermometer.	Mean Dilatation of Copper for each Degree.	Temperature by Copper Thermometer.	Mean Dilatation of Platinum for each Degree.	Temperature by Platinum Thermometer.
212°	$\frac{1}{50760}$	212°	$\frac{1}{34120}$	212°	$\frac{1}{67860}$	212°
572°	$\frac{1}{40678}$	$702^{\circ}5$	$\frac{1}{31860}$	$623^{\circ}8$	$\frac{1}{65340}$	$592^{\circ}9$

“It appears that, at temperatures beyond 212° , glass expands in a greater ratio than mercury, and as the mercurial thermometer measures the *difference* of the expansion of the glass and metal upon the supposition that they are both uniform, its degrees require a correction in the upper part of the scale, when compared with the equal dilatation of air. Thus the temperature of 586° on the mercurial thermometer corresponds with 572° on the air thermometer; while, from the third column of the first table, it appears that the expansion of glass alone, supposed to be equable, would indicate 667° for the same point. The second, fourth, and sixth columns of the second table show the mean expansion for each degree of iron, copper, and platinum when heated from 32° to 212° , compared with that from 32° to 572° ; the third, fifth, and seventh columns indicate the degrees on thermometric bars of these metals, corresponding to the temperature of 572° on an air thermometer.” (DANIELL, § 148.) By the aid of his register pyrometer, Mr. Daniell has constructed the following table, showing the progressive amount of the expansion of several metals, up to their point of fusion.

Progressive Dilatation of Solids.

1000000 PARTS, AT 62°.

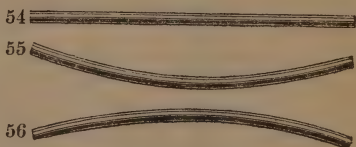
	At 212°.	At 662°.	At Fusing Point.
Black Lead Ware . .	1000244	1000703	
Wedgwood Ware . .	1000735	1002995	
Platinum	1000735	1002995	{ 1009926 maximum, but not fused.
Iron (Wrought) . . .	1000984	1004483	{ 1018378 to the fusing points of cast iron.
Iron (Cast)	1000893	1003943	1016389
Gold	1001025	1004233	
Copper	1001430	1006347	1024376
Silver	1001626	1006886	1020640
Zinc	1002480	1008527	1012621
Lead	1002323		1009072
Tin	1001472		1003798

Dr. Ure has proved, in regard to zinc, that that metal permanently elongates after frequent heating and cooling. "It would seem," he says, "that the plates composing this metal, in sliding over each other, by the expansive force of heat, present such an adhesive friction as to prevent their entire retraction." In regard to the unequal expansion of bodies at different temperatures, the same philosopher remarks, that it is probable every species of matter follows an increasing rate in its enlargement by caloric, for each portion that enters a body must weaken cohesion, and therefore render the operation of the next portion that is introduced more efficacious. The curious fact of the unequal expansion of certain crystals discovered by Mitscherlich has already been mentioned, (p. 118.)

In consequence of the extensive use which is made of iron in the construction of bridges, and as a substitute for timber, mechanics have become more fully aware of the necessity of making due allowance for its expansion and contraction, and such arrangements as may admit of it without injury to the other parts of the building. The arches of the Southwark bridge rise and fall about one inch within the usual range of atmospheric temperatures. Where great lengths of iron pipe are used, as for the conveyance of gas or water, some of the junctions are so contrived as to allow of their elongation and contraction, without fracture. Where iron beams are employed, they must be so placed as to admit of some play without injury to the walls; and where such precaution has not been taken, their contraction and expansion have tended to endanger the building. Iron roofs, in consequence of their situation exposing them to the influence of a hot sun, or to the cold of winter, require peculiar care in this respect; and in other cases, apparently of trivial importance, serious consequences have resulted from the incautious application of iron bars in situations where their changes of bulk could be productive of mischief, as in clamping stones together in the construction of steeples, and in placing iron railings between columns, &c.; for these changes of bulk, small as they are in amount, take place with irresistible force. This fact was well illustrated in an application made of it by M. Molard for restoring the perpendicularity of the walls of the Museum

of Arts and Manufactures in Paris, which, in consequence of the weight of the roof, were bulging outward; he laid iron rods across the building, the ends of which projected through the opposite walls; these rods were then heated, and when in an expanded state a strong iron plate upon either end of each rod was firmly screwed up against the exterior of the wall: during their contraction on cooling the rods drew the walls somewhat nearer together: the bars were then again elongated by heat, the screws being again tightened, and so by a repetition of the process the walls were gradually brought to a perpendicular position. The same process has been applied in the restoration of the cathedral at Armagh.

It appears from the above tables that the expansion of glass and of platinum is nearly similar: hence wires of that metal may be welded into fused glass without inconvenience; but if we substitute a wire of another metal, its different rate of contraction will tend to break the glass as it cools. It is also seen that iron or steel is less expansible than brass; if, therefore, we form a compound bar of these or any other two differently expansible metals, by riveting or soldering them together, such a bar, by changes of temperature, will constantly warp in one direction or other, according to the relative position of the steel and brass. Let fig. 54 represent the compound bar, the steel being uppermost; if we then put it upon a heated plate, the bar will warp, as shown in fig. 55, in consequence of the greater expansion of the brass; if, on the contrary, the compound bar be subjected to cold, it will assume the opposite curve, fig. 56, in consequence of the greater contraction of the brass. A compound plate of silver and platinum is remarkably susceptible of these contortions; and such contrivances have been applied to the construction of instruments for measuring changes of temperature, as in *Breguet's Thermometer*, which consists of a very thin and narrow strip of platinum, plated with silver and coiled into a spiral, one end of which is attached to an upright support, and the other to an index moving over a graduated circle: with changes of temperature the spiral twists and untwists, carrying with it the index: the value of the degrees on the circle is determined by comparison with a mercurial thermometer.



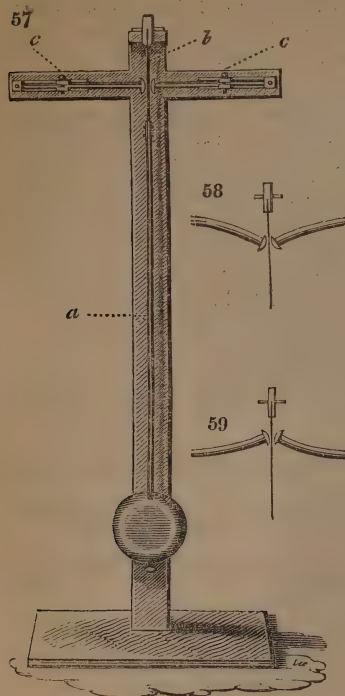
The expansion and contraction of the metals by heat and cold is a serious inconvenience to the chronometer-maker, as necessarily interfering with the rate of going of the clock or watch. The pendulum, to vibrate seconds, must always be of a given length*, and it is obvious that if of metal it will be liable to shorten in winter and lengthen in summer: thus the clock will be fast in the former, and slow in the latter season†.

* The length of the pendulum vibrating seconds in *vacuo* in the latitude of London ($51^{\circ} 31' 8''$ North) at the level of the sea, and at the temperature of 62° , is = 39.13929 inches of Sir George Shuckburgh's standard scale. KATER, *Phil. Trans.*, 1819, p. 415.

† When the bob is let down $\frac{1}{100}$ of

an inch, the clock loses ten seconds in twenty-four hours; hence the elongation of $\frac{1}{1000}$ of an inch will cause it to lose one second per day, and a change of temperature equal to 30° of Fahrenheit will alter its length about $\frac{3}{5000}$ part, and occasion an error in the rate of going, of eight seconds per day.

The contrivances which have been resorted to, to counteract this inconvenience, are numerous, and many of them extremely ingenious;



but any details upon the subject would be misplaced here. The following mode of compensation is, however, particularly illustrated by the principle here explained. *a* represents the pendulum-rod of brass or steel, suspended by the thin plate *b* between the compensation-bars of brass and steel (fig. 54) *c c*, which are firmly fixed at the ends *c*, and are supplied with proper adjustments. Let us now suppose the pendulum exactly vibrating seconds at the temperature of 62° , and that the temperature rises to 80° : in this case, the bar *a* would be elongated, and it would not then vibrate so many as 60 seconds in the minute; but the effect of increase of temperature in the compensation-bars, supposing the brass uppermost, would be to warp them, as in the annexed sketch, fig. 58, and, virtually, to shorten the pendulum; and in cold weather, on the contrary, the rod of the pendulum would be shortened, but the bars warping upwards (as in fig. 59,) would tend to elongate it. A similar plan

of compensation may be applied to the balance-springs of watches, which are affected in the same way, and with the same effects, as the pendulum of a clock.

The dimensions of wood are much less altered by changes of temperature than those of metals; it is, therefore, occasionally used for the rods of very large pendulums; but, in other cases, it is not found effectual, and is liable to be deranged by the varying moisture of the atmosphere.

There are some common operations, in which the expansion and contraction of metals by heat and cold are beneficially applicable: by putting the hoops upon a cask, in a heated state, they gradually contract on cooling, and firmly bind the staves together; and, with the same view, the wheelwright heats the tire of his wheel, that it may firmly press upon the circumference as it cools: so also the plates of large boilers are united by hot rivets, which during their contraction on cooling draw them firmly and securely together.

A very remarkable anomaly as regards the usual laws of expansion and contraction is presented by the fusible alloy of two parts of bismuth, one of lead, and one of tin. A bar of this metal at 32° expands till it attains the temperature of 111° ; it then rapidly contracts by the continued addition of heat up to 156° , when it has attained its maximum density, occupying less space than even at 32° ; it then again progressively

expands, its point of fusion being 201° . (ERMANN.) These extraordinary phenomena are well illustrated by filling a glass test-tube with the fused alloy, and suffering it to cool; this goes on quietly till it arrives at its minimum volume, 156° ; soon after which the tube is suddenly broken by the expansion of the metal during cooling, it attaining its maximum volume at 111° .

§ 3.—EXPANSION OF LIQUIDS.

THE expansibility of different liquids, like that of solids, is liable to variation: ether, for instance, is more expandible than alcohol, and alcohol more so than water, and water than mercury. Liquids are also differently expandible at different temperatures; and, generally speaking, their rate of expansion increases with their temperature. This irregularity is chiefly observed in those liquids which readily boil; where they require a very high temperature to convert them into vapour, it is less observable. The expansion of mercury, for instance, at low and high temperatures, is only slightly dissimilar; hence one of its great advantages in the construction of thermometers. The following Table, by Dr. Thomson, shows the rate of expansion of several liquids between the temperatures of freezing and boiling water.

Temp.	Mercury.	Linseed Oil.	Sulphuric Acid.	Nitric Acid.	Water.	Oil of Turpentine.	Alcohol.
32°	100000	100000	—	—	—	—	100000
40	100081	—	99752	99514	—	—	100539
50	100183	—	100000	100000	100023	100000	101105
60	100304	—	100279	100486	100091	100460	101688
70	100406	—	100558	100990	100197	100993	102881
80	100508	—	100806	101530	100332	101471	102890
90	100610	—	101054	102083	100694	101931	103517
100	100712	102760	101317	102620	100903	102446	104162
110	100813	—	101540	103196	—	102943	—
120	100915	—	101834	103776	101404	103421	—
130	101017	—	102097	104352	—	103954	—
140	101119	—	102320	105132	—	104573	—
150	101220	—	102614	—	102017	—	—
160	101322	—	102893	—	—	—	—
170	101424	—	103116	—	—	—	—
180	101526	—	103339	—	—	—	—
190	101628	—	103587	—	103617	—	—
200	101730	—	103911	—	—	—	—
212	101835	107250	—	—	104557	—	—

According to Mr. Graham, on being heated from 32° to 212°

Alcohol expands $\frac{1}{6}$, that is 9 measures become 10

Fixed oil . . . $\frac{1}{12}$. . . 12 13

Water . . . $\frac{1}{22 \cdot 76}$. . . 22·76 23·76

Mercury . . . $\frac{1}{55 \cdot 5}$. . . 55·5 56·5

Alcohol, therefore, is six times more expansive by heat than mercury; and in the height of summer spirit of wine will measure about 5 per cent. more than in the depth of winter.

The expansibility of the liquids resulting from the compression of gases is extremely remarkable, for it appears from the experiments of

M. Thilorier (*Ann. de Chim. et Phys.*, LX., 427) that fluid carbonic acid is even more expansible by heat than air; heated from 32° to 86° , twenty volumes of this liquid increase to twenty-nine, which dilatation is about four times greater than that of air. Mr. Kemp has extended this observation to the liquids resulting from the compression of sulphurous acid and of cyanogen, which, though less dilatable than carbonic acid, are much more so than common liquids.

A remarkable correspondence has been observed by Gay Lussac between the rates of expansion of alcohol and sulphuret of carbon, although their boiling points are very different, that of alcohol being 173° , and of sulphuret of carbon 116° : their changes of bulk for changes of temperature are stated to be precisely similar, and they are the only liquids known to possess such a relation.

There is an extraordinary exception to the law of expansion and contraction by heat and cold, in the case of *water*, which, unlike other fluids, *expands when cooled below a certain point**. Other fluids diminish in bulk till they freeze; but if we fill a large thermometer-tube with water, of the temperature, for instance, of 80° , and then plunge the bulb into a freezing mixture, the water goes on shrinking till it has attained the temperature of about 40° ; and then, instead of continuing to contract till it freezes, (as is the case with other liquids,) it slowly expands and rises in the tube until it congeals. In this case the expansion below 40° and above 40° seem to be equal; so that water will be of the same bulk at 32° as at 48 , that is, at 8° degrees above or below 40° . Crichton's experiments place the maximum of density at 42° , (*Ann. of Phil.*, N.S., v., p. 491;) those of Hallström at 39.4 , (*Ann. de Chim. et Phys.*, xxviii., p. 90.) There is an elaborate paper in the *Ann. de Chim. et Phys.* (t. LXX.) by Despretz, upon the maximum density of water and of saline solutions: he places the maximum density of water at $+4^{\circ}$ Centigrade, and states that below the maximum density the dilatation by cold is more considerable than the dilatation by heat above the same point, but that the difference is very minute and may probably be fallacious: that sea water and all saline solutions have a maximum of density: that the maximum of density sinks more rapidly than the point of congelation.

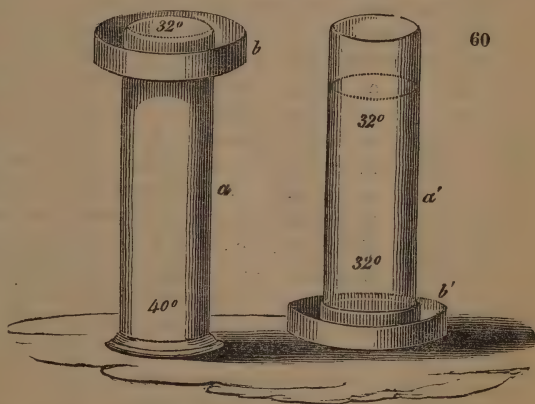
The anomalous expansion of water by cold is productive of some most important consequences in nature; for if water, like other fluids, went on diminishing in bulk, and therefore increasing in density, till it froze, large bodies of water, instead of being only superficially frozen in winter, would become solid masses of ice. Let us take a fresh-water lake as an example. The earth being warmer in winter than the air, the heat is withdrawn from the *surface* of the water by the cold breezes that blow over it, and the whole body of water has its temperature lowered to 40° , *which is the point of its greatest density*, and a temperature congenial to fish and other aquatic animals. The cold now continues to operate upon the surface of the water, but instead of diminishing its bulk, and rendering it *heavier* than the warmer water beneath, it expands and renders it *lighter*; so that, under these circumstances, a stratum of ice-cold water (at 32°) will be found lying upon a mass of warmer water beneath it (at 40°). The influence of the cold continuing, the surface of

* See Prefatory History, p. 44.

the lake will soon freeze, but the water immediately below the superficial coating of ice will be found comparatively warm; and as water is almost a non-conductor of heat, it will be a long time before the ice attains any thickness; and the whole body of water, if of any depth, can never freeze throughout. Indeed, it will be obvious that the retardation of freezing will be proportional to the depth of water which has to be cooled, and hence some very deep basins or lakes are scarcely ever covered with ice.

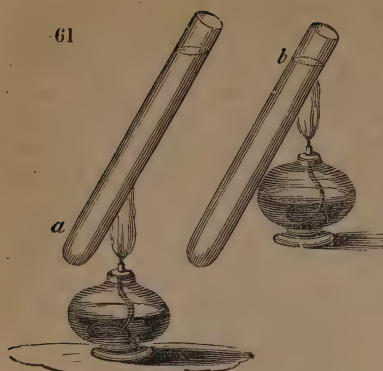
Perhaps the following experiment may render this property of water more intelligible. Let a a' , fig. 60, represent two cylindrical glass vessels, filled with water at 60° ; b b' are tin trays surrounding and closely fitting the exteriors of the cylinders, and intended to contain a freezing mixture of snow and salt, which in a is applied to the upper *surface*, but in a' to the *bottom* of the water. The first effect of the cold will be to reduce the temperature of the whole bulk of water, in both vessels, to 40° ,

that is, to the point of greatest density. After which it will be found that, in the vessel a , the cooling effect will not proceed downwards, but will be limited to the surface, where the thermometer will gradually fall to 32° , and the water probably freeze; for the ice-cold water being lighter than the water at 40° below,



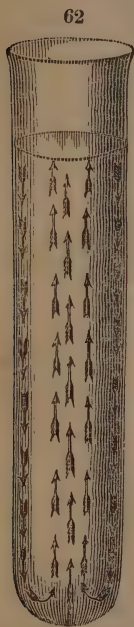
it will necessarily float upon the surface: a thermometer, therefore, in the upper part of the vessel will fall to 32° , but in the lower part only to 40° . This may be said to represent the case of the lake above described. In the second cylinder a' , the cold, instead of being applied to the surface of the water, is applied to the bottom, and the effect is very different; for now the cooled water becoming lighter, ascends, whilst the warmer water descends, and becoming cooler in its turn, the whole body of water is reduced to the freezing temperature, an effect limited to the *surface* in the other cylinder, which represents what happens in nature, where the cold is always superficial; and ice being lighter than water, it is, of course, formed and remains upon the surface. With respect to sea water, or to a solution of salt in water, it is found that the temperature of the maximum of density becomes lower and lower in proportion to the quantity of salt dissolved.

As liquids, generally speaking, are *enlarged*, and consequently rendered *specifically lighter*, by heat, it follows that, in heating a mass of liquid, very different effects will be produced by applying heat to different parts of the vessel containing it: a and b , fig. 61, represent two tubes of thin glass filled with water. If we apply the flame of the spirit-lamp to the *bottom* of



the tube *a*, the water will soon be heated equally throughout, and boil; and this is the usual way of applying heat, namely, to the bottom of the boiler; but if, as in the tube *b*, we heat the *surface* of the water, we shall find that it may be made to boil in the upper part of the tube, whilst the water at bottom will remain cold. In this case, the water becomes *lighter* by being heated, and consequently floats upon the colder water below, to which scarcely any heat will be communicated.

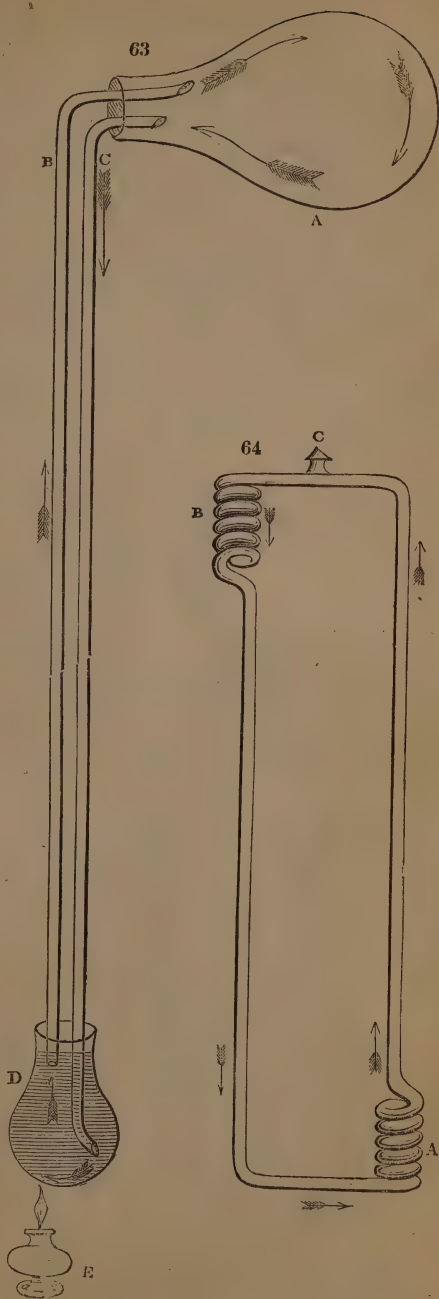
The currents that ensue, in the ordinary way of heating water, may be rendered obvious by the following experiment:—Fill a cylindrical glass vessel, of the shape annexed, fig. 62, with water, and throw into it a few particles of bruised amber, or any other convenient substance, nearly of the same specific gravity as the water,



so that, if possible, they may neither sink nor float in it; then apply a gentle heat to the centre of the *bottom* of the vessel, and it will be seen that currents immediately begin to ascend in the centre, or axis, and to descend towards the circumference of the vessel, in the direction shown by the darts, or in an inverted direction if the *sides* of the tube are most heated. These currents soon become rapid, and continue till the water boils. It is, therefore, by changes in the specific gravity of the different portions of water, that we succeed in conveying heat throughout the mass. The heated portion becomes enlarged, and, therefore, specifically lighter than the adjacent cold portions through which it ascends; whilst they, descending, come into the contact of the heated surface, and in their turn expand and rise. This goes on till the whole of the water has acquired its boiling temperature, and the currents then cease. Such currents may be established, in properly-constructed vessels, to any extent, and heat thus communicated to water at a considerable distance from the boiler; a system lately adopted very advantageously in heating houses, conservatories, manufactories, and baths. The contrivances for these purposes are very various; but all, of course, imply the necessity of an *ascending* and *descending* current. The annexed (fig. 63) is a form of apparatus employed by Mr. Faraday for the illustration of the direction and extent of these currents, and their application to the conveyance of heat from one place to another. *A* is a large glass flask filled with water, into which the tubes *B C* are tightly fitted by a perforated cork and cement; these tubes are also filled with water, and dip into the flask *D*, which is filled with water deeply tinged blue with indigo; the tube *B* dipping only about half an inch below the surface,

whilst *c* descends nearly to the bottom of the blue liquor, and should be very slightly curved upwards at its extremity. On applying the flame of a spirit lamp, as at *E*, the blue liquid ascends by the tube *B* and circulates through *A*, the water from which descends through *c* into *D*, and thus a circulation of the fluid is kept up and the heat conveyed from one flask to the other.

In Mr. Perkins's apparatus for conveying heat through buildings by the circulation of water, an endless tube is employed, the surface of which is occasionally increased by spiral or other turnings where the heat is to be given off or acquired: the annexed figure (64) may serve to illustrate this principle; it represents a very strong iron tube of about one inch diameter completely filled with water; the spiral *A* passes through a furnace where it is highly heated, and the water is consequently put into motion in the direction of the arrows; the boiling of the water or formation of steam is prevented by the pressure, whence the necessity of the extreme perfection and strength of the tube. *B* represents a second coil which is supposed to be in an apartment where the heat is to be given out. *c* is a screw stopper by which the water may be occasionally replenished. By this form of apparatus the water may be heated to 300° or 400° , or even higher, so as occasionally to singe paper. A larger tube and lower temperature are, however, generally preferable.



§ 4.—EXPANSION OF AERIFORM BODIES AND VAPOURS.

WE may now notice *the effects of heat upon gases, air, and vapours*. These undergo much greater relative changes of bulk than the other forms of matter, but they also present an important peculiarity. In other substances, each individual has its own degree of expansion and contraction, whereas *all pure æriform bodies expand and contract alike*: so that, if we accurately determine the expansion and contraction of any one of them, in a given range of temperature, that knowledge applies to all the rest. It has been ascertained by Dalton and Gay Lussac that 1000 measures of air, when heated from the freezing to the boiling point of water, suffer an increase in bulk equal to 375 parts; so that 1000 cubic feet of air, at 32°, become dilated to 1375 cubic feet at 212°. Air, therefore, at the freezing point, expands $\frac{1}{480}$ th part of its bulk for every added degree of heat on Fahrenheit's scale: that is,

480 cubic inches, at 32°, become
481 ——— at 33°,
482 ——— at 34°, &c.

increasing one cubic inch for every degree. A contraction of one cubic inch occurs for every degree below 32°: thus

480 cubic inches, at 32°, become
479 ——— at 31°,
478 ——— at 30°, &c. (GRAHAM.)

Air, therefore, at 32° has its volume doubled at 480°, and tripled at 960°: the latter temperature is about that of a dull red heat. Steam, and all other vapours, when heated out of contact of their respective fluids, are subject to laws of expansion similar to those of air. The following table shows the changes of bulk suffered by 100,000 parts of air at all temperatures between 32° and 212°.

Temp.	Bulk.	Temp.	Bulk.	Temp.	Bulk.	Temp.	Bulk.	Temp.	Bulk.
32°	100000	49°	103536	65°	106864	81°	110192	97°	113520
33	100208	50	103749	66	107072	82	110400	98	113728
34	100416	51	103952	67	107280	83	110608	99	113936
35	100624	52	104166	68	107488	84	110816	100	114144
36	100833	53	104368	69	107696	85	111024	110	116224
37	101040	54	104576	70	107904	86	111232	120	118304
38	101248	55	104791	71	108112	87	111440	130	120384
39	101459	56	104992	72	108320	88	111648	140	122464
40	101666	57	105200	73	108528	89	111856	150	124544
41	101872	58	105408	74	108736	90	112064	160	126624
42	102080	59	105616	75	108944	91	112272	170	128704
43	102290	60	105824	76	109152	92	112480	180	130784
44	102496	61	106032	77	109360	93	112688	190	122864
45	102708	62	106240	78	109568	94	112896	200	134944
46	102916	63	106448	79	109776	95	113104	210	137024
47	103124	64	106656	80	109984	96	113312	212	137440
48	103333								

The rate of expansion of atmospheric air at temperatures *above* 212° has been investigated by Dulong and Petit (*Ann. de Chim. et Phys.*, vii. 120). The following table exhibits the results of their observations.

Temperature by the Mercurial Thermometer.		Corresponding Volumes of a given Volume of Air.
Fahr.	Centig.	
— 33	— 36	0·8650
32	0	1·0000
212	100	1·3750
302	150	1·5576
392	200	1·7389
482	250	1·9189
572	300	2·0976
680	360	2·3125

The dilatation suffered by air, when heated, being very considerable, is, of course, attended by a proportionate diminution in the specific gravity or relative weight of the heated portion, which ascends through the colder mass, and excites currents and agitations in the general bulk of air. These currents generally escape observation, in consequence of the invisibility of air; but they may easily be rendered evident; and often excite attention by their violence, as when powerful draughts and wind are produced. The smoke-jack is put into motion by the force of the current of air which passes up the chimney.

In consequence of the relative *lightness* of heated air, it always rises to the upper parts of rooms and buildings, when it either escapes, or, becoming cooled and relatively *heavier*, again descends. If, in cold weather, we sit under a skylight in a warm room, a current of cold air is felt descending upon the head, whilst warmer currents, rising from our bodies, and coming into contact with the cold glass, impart to it their excess of heat. Being thus contracted in bulk, and rendered specifically heavier, they, in their turn, descend, and thus a perpetual motion is kept up in the mass of air. This effect is attended with much inconvenience to those who inhabit the room, and is in great measure prevented by the use of double windows, which prevent the rapid cooling and production of troublesome currents in the air of the apartment.

We generally observe, when the door of a room is opened, that there are two distinct currents in the aperture, which may be rendered evident by holding in it the flame of a candle. At the upper part it is blown outwards, but inwards at the lower part; in the middle, scarcely any draught of air, one way or other, is perceptible.

The art of *ventilating* rooms and buildings is, in a great measure, dependent upon the currents which we are enabled to produce in air by changes of temperature, and is a subject of considerable importance. As the heated air and effluvia of crowded rooms pass upwards, it is common to leave apertures in or near the ceiling for their escape. Were it not, indeed, for such contrivances, the upper parts of theatres and of some other buildings would scarcely be endurable; but a mere aperture, though it allows the foul air to escape, in consequence of its specific lightness, is also apt to admit a counter-current of denser and cold air, which pours down into the room. This effect is prevented by heating, in any convenient way, the tube or flue through which the foul air escapes. A constantly ascending current is then established; and whenever cold air attempts to descend, the heat of the flue rarefies and drives it upwards. Thus the different ventilators may terminate in tubes connected with a chimney; or they may unite into a common trunk, which may pass over

a furnace purposely for heating it; or heated air may be sent, by a flue from below, into the space between the roof and ceiling of the room to be ventilated, and it may have free escape by proper apertures.

In some of our theatres, the gas-chandelier is made a very effectual ventilator. It is suspended under a large funnel, which terminates in a cowl outside the roof; and the number of burners heat the air considerably, and cause its very rapid and constant ascent through the funnel, connected with which there may be other apertures in the ceiling of the building. But in these and similar cases, we often observe that the vents are not sufficiently capacious; and the foul air from the house, and from the gas-burners themselves, not being able readily to escape, diffuses itself over the upper part of the building, and renders the galleries hot and suffocating, all which is easily prevented by the judicious adjustment of the size of the ventilating channels to the quantity of air which it is requisite should freely pass through them. The small tin ventilators, consisting of a rotating wheel, which we sometimes see in window-panes, are perfectly useless, though it is often imagined, in consequence of their apparent activity, that they must be very effectual; but the fact is, that a very trifling current of air suffices to put them in motion, and the apertures for its escape are so small as to produce no effectual change in the air of the apartment: they are also as often in motion by the ingress as by the egress of air.

From what has been said, it will be obvious that our common fires and chimneys are most powerful ventilators, though their good services in this respect are often overlooked. As soon as the fire is lighted, a rapid ascending current of air is established in the chimney, and consequently there must be a constant ingress of fresh air to supply this demand, which generally enters the room through the crevices of the doors and windows. When these are too tight, the chimney smokes, or the fire will not draw; and in such cases it is sometimes necessary to make a concealed aperture in some convenient part of the room for the requisite admission of air, or to submit to sitting with a window or door partly open. Any imperfect action of the chimney, or descending current, is announced by the escape of smoke into the room, and is frequently caused by the flue being too large, or not sufficiently perpendicular and regular in its construction. When there is no fire, the chimneys also generally act as ventilators; and in summer there is often a powerful current up them, in consequence of the roof and chimney-pots being heated by the sun, and thus accelerating the ascent of the air. In a well-constructed house, there should be sufficient apertures for the admission of the requisite quantity of air into the respective rooms, without having occasion to trust to its accidental ingress through every crack and crevice that will allow it to pass. These openings may either be concealed, or made ornamental, and, by proper management, may be subservient to the admission of warm air in winter. A few spare flues should also be provided which may be used either for the egress or ingress of air, independent of the chimneys, as occasion may require.

The manner in which heat is distributed through our apartments by the fires in common use will be noticed afterwards; but large rooms are not uncommonly warmed by heated air, admitted usually through apertures

in the floor. This system is convenient, effective, and agreeable, when properly managed, but this is seldom the case. The rooms are close and oppressive, because due *ventilation* is not associated with the admission of the hot air; the apertures by which the air is admitted are generally too small, and the air itself overheated: the openings should be, according to circumstances, either large, or very numerous, and the *quantity* of air thrown in should be *considerable*, but its *temperature moderate*. In this way the bad smell produced by burnt particles of dust is avoided, and an agreeable freshness, as well as temperature, kept up in the air.

§ 5.—OF THE DETERMINATION OF SPECIFIC GRAVITIES.

FROM the changes of bulk which bodies sustain when they change their temperature, it is obvious that their relative *densities* or *specific gravities* will be liable to proportionate changes; hence chemists are in the habit of referring these to the mean temperature of 55° or 60° , and as the bulk of æriform bodies is also subject to change by increased or diminished pressure, their densities are compared not only at mean *temperature*, but also at mean *barometrical pressure*.

By the term *specific gravity*, we mean the ratio of *weight* to *bulk*; the object, therefore, of the processes for ascertaining it, is either to determine the *weight of a known bulk*, or the *bulk of a known weight*; for whether the substances be reduced to the same weight, and then measured, or to the same bulk, and then weighed, the ratio of their weights to their bulks will be discovered. If reduced to the same bulk, and weighed, their specific gravities will be *directly* as the weights; if reduced to the same weight and measured, their specific gravities will be *inversely* as their bulks. Suppose a like bulk of each kind of matter in nature to be weighed, the results, numerically stated, would represent their specific gravities. But as this would be inconvenient, and often impossible, another method of reducing their bulks to a common measure is resorted to; and, in the case of solids and liquids, the specific gravity of pure water is assumed as the unit to which their specific gravities are compared. On dividing the weight, for instance, of any bulk of the metal *zinc* by the weight of a like bulk of water, the quotient is 7; this, therefore, is said to be the specific gravity of zinc. Proceeding in the same way with *silver*, the quotient is 10·47; with *gold*, 19·3; with *potassium*, 0·86; with *sulphuric acid*, 1·85; with *alcohol*, 0·80: hence these numbers are considered as representing the specific gravities of those bodies; that is, they are their relative weights to water, all being of the same temperature. To obtain the specific gravity, therefore, of a body, we divide its weight by the weight of a quantity of pure water equal to it in bulk, and this we determine as follows:—

We use a delicate balance*, so contrived as to admit of substances

* Balances fitted up for the purpose of ascertaining specific gravities are sold by the philosophical instrument makers: in regard to their use, and the precautions requisite in the various steps of the process, see FARADAY'S *Manipulation*, § II.

“Equality in the length of the arms of

the lever is, of course, the most important consideration in the construction of the balance; but when there may be any reason to doubt this essential point, it is well to know that any error may be avoided by the method of *double weighing*. This consists in placing the object whose

being attached to one of the scales by means of a horse-hair or a fine thread of silk. The absolute weight of the body thus suspended is then very carefully ascertained: it is next immersed in distilled water, of the temperature of 60° ; and the beam being again brought to an equilibrium, we learn the weight lost by its immersion; or, in other words, we ascertain the weight of its bulk of pure water. We now divide the sum of its absolute weight by that of the weight which it lost in water, and the quotient is its *specific weight*, or gravity, compared with water of the temperature of 60° .

Suppose a substance, weighing 360 grains, to lose 60 by immersion in water, the specific gravity of that substance will be $= 6$; for $360 \div 60 = 6$.

When the substance, whose specific gravity is to be ascertained, is *lighter* than water, it may be suspended with some heavier body, and, having determined the weight of the former in air, and of the latter in water, we fasten them together by means of a fine thread (not so closely as to exclude water from their contiguous surfaces, or to include air-bubbles), and weigh them in water, when it will be found that their aggregate weight will fall short of that of the heavier body. If we now subtract the weight of the lighter body from that of the heavier body, and add the remainder to the weight of the former in air, we obtain the weight of a quantity of water equal in bulk to the lighter body; we then divide the weight of the lighter body in air by this last-mentioned sum, and the quotient is its specific gravity.

"A piece of elm wood, having been varnished over to prevent its absorbing water, was found to weigh 920 grains in *air*; a piece of lead, chosen as the ballast, was ascertained to weigh 911.7 grains in *water*; the elm and lead were then tied together, and were found to weigh, in *water*, only 331.7 grains, being 580 grains less than the weight of the lead alone; therefore 580 were added to 920, that is, to the weight of the elm in air, which made up the sum of 1500: lastly, 920 were divided decimally by 1500, and the quotient, .6133, gave the specific gravity required."—Dr. PARIS: *Med. Chem.* 9.

When the substance, whose specific gravity is required, is *soluble* in water, some other fluid, of known specific gravity, must be used, which does not act upon it; alcohol, oil of turpentine, or olive oil, may, in most instances, be used, or in some cases the substance may be coated with varnish. When the substance is in *powder*, it may generally be weighed in a specific-gravity bottle.

For ascertaining the specific gravity of liquids, we usually employ a thin phial, holding 1000 grains of distilled water, at the temperature of 60° . If filled with any other liquid, and weighed, we learn its specific gravity; thus we should find that it would contain 13,500 grains of mercury; 1845 grains of sulphuric acid; 1420 grains of nitric acid, &c., which numbers of course represent the specific gravities of those liquids.

weight is to be ascertained in one scale-pan and exactly counterbalancing it in the other, not with the weights, but with sand or shot, or any other indifferent substance. The substance is then removed, and the weights applied in the same pan till the counterpoise is ba-

lanced. By this contrivance the unknown quantity of matter is compared with the known, under exactly equal circumstances, and the result is independent of almost every source of error which can affect the comparison of one object with another."—DANIELL, § 32.

A bottle, however, holding 1000 grains, is often inconveniently large, and a small and thin globular phial, with a piece of thermometer-tube ground into it by way of stopper, will be found more useful: such a phial should not weigh more than from 50 to 60 grains, and may contain between 400 and 500 grains of water. To use it, it should be accurately counterbalanced in a delicate pair of scales, and then filled with distilled water, and the stopper thrust in, the capillary opening in which allows a little to ooze out, and prevents the likelihood of bursting the phial; it is then to be wiped clean and dry, and again carefully weighed, by which the quantity of water it contains is ascertained; the water being poured out, it is next filled with the liquid whose specific gravity is required, taking care that it is of the same temperature as the water; we then weigh as before, and divide the weight of the liquid by the former weight of water; the product gives the specific gravity required. Thus, suppose the phial to contain 425 grains of water at the temperature of 60° , it will be found to hold 5737·5 grains of pure mercury of the same temperature; and $5737\cdot5 \div 425 = 13\cdot5$, the specific gravity of mercury. Or, supposing the liquid lighter than water, such as alcohol, of which we may assume the phial to contain 350·5; then $350\cdot5 \div 425 = 0\cdot824$, the specific gravity of the alcohol under trial.

We also, in determining the specific gravity of fluids, frequently employ the *hydrometer*; but it cannot be resorted to where great accuracy is required. Where, however, a number of specific gravities are to be quickly determined, as in respect to spirituous liquors for the purpose of levying duties, or in certain processes of the arts, these instruments, from the facility of their application, become indispensable.

The determination of the specific gravity of air, and of different gases, will be described under the article *Atmospheric Air*, as it involves several circumstances not yet adverted to.

§ 6.—THERMOMETERS AND PYROMETERS.

HAVING stated some of the general effects of contraction and expansion, we may now proceed to the examination of the *thermometer*—an instrument of considerable importance in researches connected with the subject of heat.

The first instrument to which the term *thermometer* (from *θερμος*, *heat*, and *μητρον*, *a measure*) can properly be applied, was apparently invented by the Florentine Academicians, about the middle of the seventeenth century. It consisted of a glass tube, with a bulb or ball blown at one extremity, fig. 65, and filled up to a certain mark, with spirit of wine; the expansion of which, or its rise above the mark, indicated *heat*, and its contraction, or fall below the mark, *cold*. They afterwards placed a number of little equidistant studs of white enamel on the tube, rendering the expansions and contractions of the confined liquid more evident; and by these they sometimes divided it into a hundred parts or degrees. Such instruments were first introduced into England by Boyle. For a long time, no one would believe that a liquid could contract and expand in a tube closed at both ends; but Boyle soon satisfied himself of the



fact by experiment, and by the inspection of the *Florentine glasses*, for so these instruments were then called. About the beginning of the eighteenth century, a considerable improvement was made in this original thermometer, by Fahrenheit, of Amsterdam, who, by the use of mercury instead of alcohol, was enabled greatly to diminish the size of the tube and bulb, and to measure comparatively high degrees of temperature.

But all these instruments laboured under the serious defect of entire want of agreement with each other: the division of the tube was founded on no fixed principle, but was arbitrary, and differently constructed and applied in every thermometer. It required no common ingenuity to overcome this difficulty, and to construct instruments which should agree with each other when exposed to the same temperature. This, however, was at length effected by a suggestion of Sir Isaac Newton, founded upon a discovery of Dr. Hooke, who observed, that when a thermometer-tube, properly filled with mercury, was plunged into melting ice or snow, the liquid metal always contracted, or fell to a certain point, at which it remained perfectly stationary till all the ice was melted. If we now mark this point upon the tube, it will be found that, whenever it is subjected to the same experiment, the quicksilver falls exactly to the same level or point, and hence this point may be called the *melting-point of ice*; and it has since been ascertained that this is also precisely the point at which water, under ordinary circumstances, freezes, so that it is also called the *freezing-point of water*. Here, then, a part at least of the difficulty above adverted to is removed, and *one* fixed point for thermometric graduation ascertained.

Dr. Hooke afterwards made a similar discovery in regard to boiling water, which, under ordinary circumstances, he found always exhibited one and the same degree of heat. If, therefore, we now plunge the thermometer, upon which the freezing-point of water has already been marked, into an open vessel of water placed upon the fire or over a lamp, we shall observe the mercury continue to rise in the tube until the water boils, when it becomes quite stationary, and the point may be marked as before. Now it will be found, that whenever this thermometer is put into boiling water, the mercury will rise to the same height*. Here, then, we have a *second* determinate point, namely, the *boiling-point of water*; and it is now obvious, that if we divide the space of the tube between these two fixed points into any given number of degrees, the mercury will indicate the same degree in all bodies of one and the same temperature; and that any number of thermometers, carefully constructed upon this principle, will agree with each other in their indications of temperature.

The space between the boiling and freezing of water has often been divided into *one hundred* equal parts—the freezing point being marked 0° , and the boiling-point 100° . This is commonly called the *centigrade scale*; it originated with Celsius in Sweden, and is used in France and many other parts of Europe. *Reaumur's scale* calls the freezing-point 0° , and the boiling-point 80° , and is employed in most parts of Germany

* Some circumstances affect the boiling-point, such as the state of the barometer or of the pressure of the atmosphere, and the nature of the vessel in which the experiment is made. We presume above that the barometer stands at thirty inches, and that the vessel is of thin metal.

and Italy. In this country we generally refer to *Fahrenheit's scale*, which sets out at the temperature produced by mixing snow with salt, which is 32° below the freezing of water; and the space between that and the boiling-point being divided into 180° , the latter is called 212° . In all these scales, the graduation is continued below 0° in the same way as above it. These are called *degrees below 0°* , and are generally distinguished by prefixing the mark ($-$) *minus* before them: thus -10° means ten degrees below 0° ; sometimes the mark ($+$) *plus* is prefixed to the degrees above zero, as $+10^{\circ}$, or ten degrees above 0° .

Each degree of Fahrenheit's scale is equal to $\frac{4}{9}$ of a degree on Reaumur's: if, therefore, the number of degrees of Fahrenheit's scale, above or below the freezing of water, be multiplied by 4, and divided by 9, the quotient will be the corresponding degree of Reaumur.

Fahrenheit.	Reaumur.
$68^{\circ} - 32^{\circ} = 36 \times 4 = 144 \div 9 = 16^{\circ}$	
$212^{\circ} - 32^{\circ} = 180 \times 4 = 720 \div 9 = 80^{\circ}$	

To reduce the degrees of Reaumur to those of Fahrenheit, they are to be multiplied by 9, and divided by 4.

Reaumur.	Fahrenheit.
$16^{\circ} \times 9 = 144 \div 4 = 36^{\circ} + 32^{\circ} = 68$	
$80^{\circ} \times 9 = 720 \div 4 = 180^{\circ} + 32^{\circ} = 212$	

Every degree of Fahrenheit is equal to $\frac{5}{9}$ of a degree on the Centigrade scale; the reduction, therefore, is as follows:—

Fahrenheit.	Centigrade.
$212 - 32 = 180 \times 5 = 900 \div 9 = 100^{\circ}$	
Centigrade.	Fahrenheit.
$100 \times 9 = 900 \div 5 = 180 + 32 = 212^{\circ}$	

The annexed scale, including De Lisle's thermometer, which is sometimes used in Russia, and in which the boiling point is marked 0° , and the freezing 150° ; and the following table of Fahrenheit's degrees compared with those of the Centigrade and Reaumur's scale, will save the trouble of their calculation.

TABLE OF THE CORRESPONDING DEGREES ON THE SCALES OF FAHRENHEIT, REAUMUR, AND CELSIUS, OR CENTIGRADE. (From Warrington's Tables.)

Fahr.	Reau.	Cent.	Fahr.	Reau.	Cent.	Fahr.	Reau.	Cent.
212	80	100	149	52	65	50	8	10
203	76	95	140	48	60	41	4	5
194	72	90	131	44	55	32	0	0
185	68	85	122	40	50	23	- 4	- 5
176	64	80	113	36	45	14	- 8	-10
167	60	75	104	32	40	5	-12	-15
158	56	70	95	28	35	- 4	-16	-20
			86	24	30	-13	-20	-25
			77	20	25	-22	-24	-30
			68	16	20	-31	-28	-35
			59	12	15	-40	-32	-40

Fahrenheit.	Centigrade.	Reaumur.	De Lisle.
210	100	80	0
200			+0
190	90	70	20
180	80		30
170		60	40
160	70		50
150		50	60
140	60		70
130		40	80
120	50	30	90
110		20	100
100	40		110
90		10	120
80	30		130
70		0	140
60	20		150
50		-10	160
40	10		170
30		-20	
20	-10		
10		-30	
0	-20		

It is very much to be regretted that, for want of a little exertion and unanimity amongst the philosophers of Europe, these discrepant thermometric scales are so inconveniently retained: the Centigrade scale is perhaps that which it would be most convenient generally to adopt. To avoid the inconvenience of the magnitude of its degrees, and the consequent necessity of frequent reference to their fractional parts, a scale has been proposed, the extremes of which are the freezing and boiling points of mercury, the former to be 0° , the latter 1000° . The entire novelty of such a scale is its principal objection.

For all common purposes ordinary thermometers are sufficiently accurate; but the experimental laboratory should be furnished with a *standard thermometer*, very carefully constructed, and with a scale exhibiting the divisions of Reaumur and Fahrenheit, and the Centigrade. Such an instrument of reference is useful to determine the quality of *common* thermometers, no two of which will be found precisely to agree at the different points of the scale. It sometimes happens that a thermometer originally correct will after a time be found to err slightly in excess in its indications of temperature, an effect probably arising from the continued pressure of the atmosphere upon the bulb, by which its bulk is permanently diminished: this may, however, be prevented by giving the bulb a certain degree of thickness, although the sensibility of the instrument to sudden changes of temperature is by this somewhat impaired.

There are numerous and useful varieties in the *forms* of thermometers, which need not be here enumerated in detail. Among them the *self-registering* thermometers are valuable, as showing the maximum and minimum of temperature during the absence of the observer. Many of these instruments which have been suggested, are too complicated or too expensive to be generally useful; but there are two of them which are sufficiently simple, and in common use, namely, Six's thermometer (*Phil. Trans.*, vol. LXXII.); and that contrived by Dr. John Rutherford (*Edinb. Phil. Trans.*, vol. iii.).

That the degrees of the thermometer actually represent equal degrees or increments of heat, is shown by a simple experiment originally suggested by Dr. Brook Taylor. It consisted in mixing together, with due precaution, equal parts of hot and cold water; and it was found that the thermometer, applied to such a mixture, indicated the arithmetical mean between the extremes. Thus, if we mix a pound of water at the temperature of 200° with a pound at the temperature of 100° , an accurate thermometer will show in the mixture the *mean* temperature of 150° .

PYROMETERS.—The indications of the mercurial thermometer are obviously limited within the freezing and boiling points of mercury. It congeals at -39° , and boils at $+662^{\circ}$; and on the moment of its congelation it shrinks so remarkably, as to have led early experimentalists into considerable errors as to the actual cold required for the purpose. When it boils, its vapour, of course, bursts the tube. Although, therefore, the range of temperature which may be accurately measured by the expansion and contraction of mercury is very extensive, it is often requisite to measure degrees of cold below its freezing-point, and of heat above its boiling-point. Pure spirit of wine, or *alcohol*, has never been frozen,

and it is consequently used in those thermometers which are intended to indicate excessive degrees of cold; but no fluid has yet been found applicable to the construction of a thermometer capable of indicating higher temperatures than mercury. When, therefore, a degree of heat approaching to, or exceeding dull redness, is to be measured, other methods and substances must be resorted to: instruments constructed for this purpose are called *pyrometers*, from *πυρ*, *fire*, and *μετρον*, *a measure*.

Of these instruments, that suggested by Mr. Daniell seems the least exceptionable, and is not liable to those sources of fallacy which render the results obtained by *Wedgwood's clay pyrometer* so uncertain and equivocal*. The following is Mr. Daniell's description of his *Register pyrometer*. (*Introd. to Chem. Phil.*, § 146.)

"It consists of two parts, which may be distinguished as the register and the scale. The *register* is a solid bar of black-lead earthenware, highly baked. In this a hole is drilled, into which a bar of any metal, six inches long, may be dropped, and which will then rest upon its solid end. A cylindrical piece of porcelain, called the index, is then placed upon the top of the bar, and confined in its place by a ring or strap of platinum passing round the top of the register, which is partly cut away at the top, and tightened by a wedge of porcelain. When such an arrangement is exposed to a high temperature, it is obvious that the expansion of the metallic bar will force the index forward to the amount of the excess of its expansion over that of the black-lead, and that, when again cooled, it will be left at the point of greatest elongation. What is now required, is the measurement of the distance which the index has been thrust forward from its first position; and this, though in any case but small, may be effected with great precision by means of the *scale*.

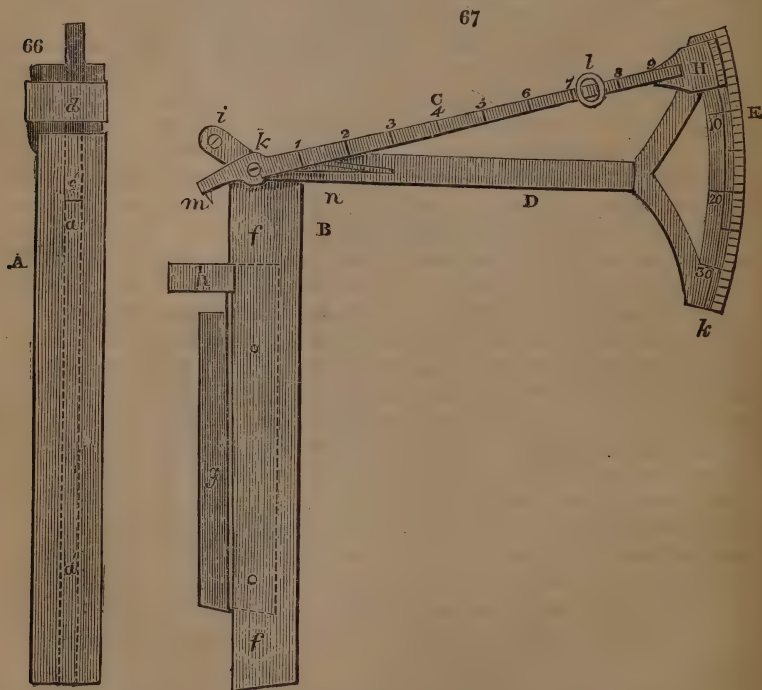
"This is independent of the register, and consists of two rules of brass, accurately joined together at a right angle by their edges, and fitting square upon two sides of the black-lead bar. At one end of this double rule a small plate of brass projects at a right angle, which may be brought down upon the shoulder of the register, formed by the notch cut away for the reception of the index. A moveable arm is attached upon this frame, turning at its fixed extremity upon a centre, and at its other, carrying an arc of a circle, whose radius is exactly five inches, accurately divided into degrees and thirds of a degree. Upon this arm, at the centre of the circle, another lighter arm is made to turn, one end of which carries a nonius with it, which moves upon the face of the arc, and subdivides the former graduation into minutes of a degree; the other end crosses the centre, and terminates in an obtuse steel point, turned inwards at a right angle.

"When an observation is to be made, a bar of platinum, or malleable iron, is placed in the cavity of the register, the index is to be pressed down upon it, and firmly fixed in its place by the platinum strap and porcelain wedge. The scale is then to be applied by carefully adjusting the brass rule to the sides of the register, and fixing it by pressing the cross piece upon the shoulder, and placing the moveable arm, so that the steel point of the radius may drop into a small cavity made for its

* This pyrometer may now be considered as obsolete. It is described in | the *Philosophical Transactions*, vols. LXXii, LXXiv, LXXvi.

reception, and coinciding with the axis of the metallic bar. The minute of the degree must then be noted, which the nonius indicates upon the arc. A similar observation must be made after the register has been exposed to the increased temperature which it is designed to measure, and again cooled, and it will be found that the nonius has been moved forward a certain number of degrees or minutes. The scale of the pyrometer is readily connected with that of the thermometer by immersing the register in boiling mercury, whose temperature is as constant as that of boiling water, and has been accurately determined by the thermometer. The amount of expansion for a known number of degrees is thus determined, and the value of all other expansions may be considered as proportional.

"The melting point of cast iron has been thus ascertained to be 2786° , and the highest temperature of a good wind furnace about 3300° ; points which were estimated by Mr. Wedgwood at 20577° and 32277° respectively.



"Fig. 66 represents the register; A is the bar of black-lead; $a a'$ the cavity for the reception of the metal bar; $c c'$ is the index, or cylindrical piece of porcelain; d the platinum band, with its wedge, e .

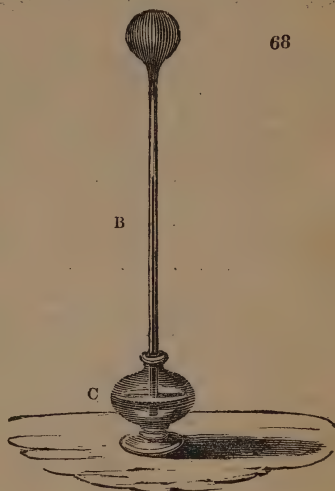
"Fig. 67 is the scale by which the expansion is measured; $f f'$ is the greater rule upon which the smaller, g , is fixed square. The projecting arm, h , is also fitted square to the ledge, under the platinum band, d . D is the arm which carries the graduated arc of the circle fixed to the

rule, ff' , and moveable upon the centre, i . c is the lighter bar, fixed to the first, and moving upon the centre, k . l is a small lens, folded back upon the arm, by which, when erected, the divisions may be accurately read off. H is the nonius at one of its extremities, and m the steel point at the other."

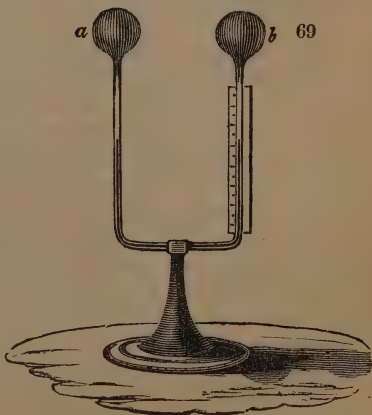
AIR-THERMOMETERS.—Sometimes the expansions and contractions of *air*, which, as already stated, are relatively great for small changes of temperature, are resorted to in delicate experiments, in which slight variations of heat require to be indicated. The simplest form of the *air-thermometer* consists of a tube with a thin bulb at its upper end, and dipping at the lower end and open extremity into a little coloured fluid, fig. 68; some of the air is then expelled by the heat of the hand, so that, as the bulb cools, the liquid may rise to about half way up the tube. This instrument is very sensible to slight changes of temperature: heat expands the air in the bulb, and drives the fluid downwards; and cold, by contracting the air, causes the fluid to rise.

This was one of the first forms of the thermometer that was invented, and is only inconvenient from its extreme delicacy, and the great length of tube required to measure any considerable range of heat and cold.

Another and much more useful form of air-thermometer is represented in the wood-cut, fig. 69: it has sometimes been called the *differential thermometer*. It consists of two



bulbs, a and b , containing air, united by a tube twice bent at right angles, in which there is a little coloured sulphuric acid: the tube is supported upon a wooden foot or stand. When a hot body is brought near one of the bulbs, it expands the air within it, and drives the fluid towards the other; from b , for instance, to a . One of the chief advantages of this air-thermometer is, that it is not affected by any general changes in the temperature of the surrounding air, because they act equally on both bulbs, and occasion no motion of the included column of liquid; but when one of the bulbs is exposed to any source of heat which does not affect the other, the *difference* of temperature between the two bulbs is immediately and very sensibly indicated by the



recession of the fluid from the heated towards the cold bulb. The advantages of this instrument will be more evident when some of its practical applications are afterwards pointed out*.

The following table from Professor GRAHAM'S *Elements of Chemistry* will give an idea of the range of temperature within which certain points have been accurately determined: the degrees are those of Fahrenheit's scale.

Greatest artificial cold produced by Thilorier	- 135°	Ice melts	+ 32°
Solid compound of alcohol and carbonic acid fuses	- 131	Medium temperature of the surface of the globe	+ 50
Greatest artificial cold produced by Walker	- 91	Medium temperature of England	+ 52
Temperature of planetary space (Fourier)	- 58	Heat of human blood	+ 98
Greatest natural cold observed by Ross	- 60	Pyroligneous spirit boils	+ 150
Ditto by Parry	- 55	Alcohol boils	+ 174
Sulphuric ether congeals	- 47	Water boils	+ 212
Mercury freezes	- 39	Tin melts	+ 442
Proof spirit freezes	- 7	Lead melts	+ 594
Mixture of 1 part of alcohol and 3 of water freezes	+ 7	Mercury boils	+ 662
Strong wine freezes	+ 20	Red Heat (Daniell)	+ 980
		Heat of common fire (do.)	+ 1140
		Brass melts (do.)	+ 1869
		Silver melts (do.)	+ 2233
		Iron melts (do.)	+ 3479

§ 6.—CONDUCTION OF HEAT.

WE have already seen (page 140) how easily heat is diffused through liquids by change of density, and that its propagation through æriform bodies is often dependent upon a similar mode of transfer (p. 142). When heat traverses *solid* bodies its passage is altogether of a different character; it suffers great retardation, and is said to be *conducted*.

It has been observed by Sir J. Herschel (*Discourse on the Study of Natural Philosophy*, p. 206), that as the particles of the most solid bodies are not absolutely in contact, conduction, when properly considered, is merely a case of radiation, and "that if we would rightly understand what is the process of nature in this slow communication of heat through the substance of a solid, we must ground our inquiries upon what takes place at a distance, and then urge the laws to which we have arrived up to their extreme case." This mutual dependence of the laws of conduction and radiation will be again adverted to when considering the latter mode of the propagation of heat. We are, however, too little acquainted with the minute corpuscular structure of bodies, to know what goes on between particle and particle, in apparent contact; and the bad radiating, yet good conducting power of the metals, apparently shows that these are distinct modes of the propagation of heat.

CONDUCTION BY SOLIDS.—A rod or bar of metal is well calculated to illustrate this conduction of heat: if one end of it be held in the candle, and the other in the hand, the heat gradually and progressively makes its way from one end to the other; if the hand be near the source of heat, or the bar short, it soon becomes too hot to hold. This slow pro-

* There is a useful treatise on the | and pyrometers in the Library of Useful
various constructions of thermometers | Knowledge. *Natural Philos.*, vol. ii.

gress of heat along the bar is well shown by attaching several bullets or wooden balls to the side of a square bar of metal 18 or 20 inches long, at intervals of about two inches apart, by a little wax, and then heating one end of the bar over a lamp: (fig. 70.) the balls successively drop off as the heat finds its way along the bar. If we employ bars of *different* metals, it will be found that some conduct heat better than others: thus, if two similar wires, one of platinum and one of silver, be heated at one end, the heat will pervade the silver much more rapidly than the platinum; and if cones of several metals, like the one represented in fig. 71, be respectively tipped with a small piece of wax, and placed upon a heated plate of metal, the wax will melt at different periods upon the different cones, thus showing their different conducting powers.



Gold, silver, copper, and tin, are the best conductors, and nearly equal; iron, platinum, and lead, are much inferior. (INGENHOUSZ, *Jour. de Phys.*, 1789, p. 68; DESPRETZ, *Ann. de Ch. et Ph.*, vol. xxxvi., p. 422.) It does not appear, therefore, that the conducting power corresponds either with the density, the tenacity, or the fusibility of the metals. In these cases of conduction the following law is observed: if the extremity of a metallic bar be placed in communication with a constant source of heat, and we wait till it has taken up a permanent state of temperature, we shall find that for distances from the source, taken in arithmetical progression, the excess of temperature above the surrounding medium will form a geometrical progression.

Next to metals, the diamond, the topaz, and some earthy compounds, appear to have the greatest conducting power: then stony bodies, porcelain and glass, and porous earthy compounds, such as earthenware and bricks. Wood is a very bad conductor of heat; so is charcoal; and these may be held, without burning the fingers, very near the red-hot part.

The following table from the experiments of Despretz, (*Ann. de Ch. et Ph.* xxxvi., p. 422), represents the conducting powers of several substances compared with gold.

Gold 1000	Platinum . . . 381	Tin 304	Porcelain . . . 12
Silver 973	Iron 374	Lead 180	Fine clay . . . 11
Copper 898	Zinc 363	Marble 24	

From the experiments of Mayer, of Erlangen, (*Ann. de Ch.*, xxx.,) it would appear that the conducting powers of different woods is in some measure inversely as their specific gravities, as shown by the following table, but water is not a very intelligible standard of reference.

	Conducting Power.	Specific Grav.		Conducting Power.	Specific Grav.
Water	10 . . .	1.000	Oak	32.6 . . .	0.668
Ebony wood . . .	21.7 . . .	1.054	Pear tree	32.2 . . .	0.603
Apple tree . . .	27.4 . . .	0.639	Birch	34.1 . . .	0.608
Ash	30.3 . . .	0.631	Silver fir	37.5 . . .	0.495
Beech	32.1 . . .	0.692	Alder	38.4 . . .	0.484
Hornbeam	32.3 . . .	0.690	Scotch fir	38.6 . . .	0.408
Plum tree	32.5 . . .	0.687	Norway spruce . .	38.9 . . .	0.447
Elm	32.5 . . .	0.646	Lime	39.0 . . .	0.408

Porous substances used in clothing, and the natural coverings of most animals, are also bad conductors of heat; but in these and similar cases interstitial air cannot be excluded, and consequently their true conducting power is not accurately determinable. Count Rumford found that when a heated thermometer, surrounded by about an inch in thickness of confined air, took 576 seconds to cool 135° , it took 1032 seconds to cool to the same point when 16 grains of *lint* were diffused through the confined air, and 1305 seconds when the same weight of *eiderdown* was used; so that the conducting power being inversely as the times, if the power of air be = 1000, that of the lint will be = 558, and of the eiderdown = 441. The conducting power of these substances is further diminished by the closeness with which their particles are compressed, provided, that is, their texture is not too closely compacted: thus, when the same space, which in the above experiment was occupied by 16 grains of eiderdown, was filled first with 32 grains, and then with 64, the times employed in the escape of the heat from the enveloped thermometer were successively increased from 1305 seconds to 1472 and 1615 seconds.

To show the influence of mere *texture* upon conducting power, similar trials were made with raw silk, ravelings of white taffeta, and of common sewing silk; of which the first has the finest fibre, the second less fine, and the third, from being twisted and harder, is much coarser. The difference between these three modifications of the same substance was very striking; the raw silk detaining the heat for 1284 seconds, the taffeta ravelings 1169 seconds, and the silk thread only 917 seconds. *Phil. Trans.*, 1792.

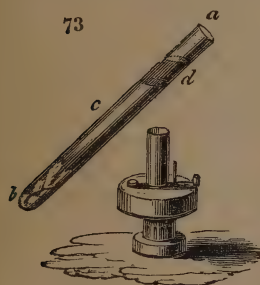
The application of these facts to the retention of the natural heat of the body by different kinds of clothing, is sufficiently obvious; and it is evident that, as far as mere conducting power of animal and vegetable substances is concerned, the worst conductors are those in which the fibres are finest and least condensed. There are, however, other circumstances which interfere in these applications, and which will be more intelligible when the subject of *radiation of heat* is under consideration.

CONDUCTION BY LIQUIDS.—Liquids are very imperfect conductors of heat, and have frequently been regarded as absolute non-conductors; the same remark applies to gaseous or æriform bodies. It has already been shown (page 140), that in the usual mode of heating liquids, the heat is applied to the *bottom* of the vessel containing them, and is diffused over the whole mass in consequence of successive *changes of density* in the heated portion; the warm currents which are thus established ascend, and the cold ones descend, and this motion is kept up till the water boils. If, however, we apply heat to the *surface* of the water, the heat can only be propagated downwards by its *conducting power*; for the heated portion, being lighter than the colder water beneath, floats upon its surface, and no interchange of strata, analogous to that previously described, can possibly ensue. It may thus be shown that it is almost impossible to transmit heat through water or other fluid by its mere conducting power. The following, among other experiments, may be selected in illustration:—Let *a*, fig. 72, represent a cylindrical vessel of water with an included air-thermometer, the bulb of which very nearly reaches the surface:

b is a small copper basin floating upon the surface, the bottom of which is only separated from the bulb of the air-thermometer by a very thin stratum of water: if some inflamed ether or alcohol, or a little glowing charcoal, be now put into the basin, the surface of the water may be heated to its boiling-point, and yet scarcely any elevation of temperature will be indicated by the neighbouring thermometer; and it will be impossible to transmit the heat from the surface downwards. In this way of making the experiment, it is obvious that some heat may be conveyed by the sides of the vessel; but as glass is a bad conductor, this source of error is comparatively small, and only produces an effect when the heat on the surface is long continued.

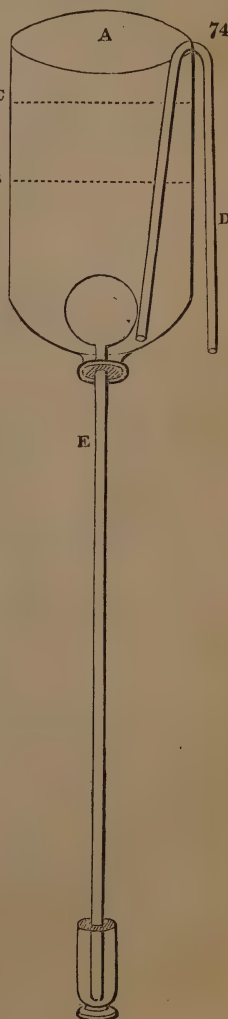
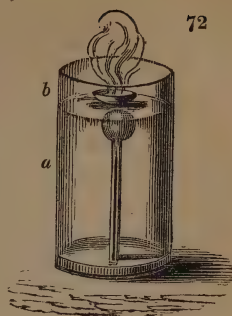
The following is a mode of illustrating the

bad conducting power of another liquid—namely *oil*. *a*, fig. 73, represents a thin glass tube about two feet in length, closed at one end, and open at the other: pour into it a couple of inches of water, and freeze it by immersion in a mixture of salt and ice;



then upon the lump of ice at the bottom, *b*, pour eight or ten inches of oil, *c*, and upon the oil, two or three inches of spirit of wine, *d*. If the portion of the tube containing the spirit be now carefully held over the chimney of a lamp, the spirit may be boiled, and even entirely evaporated, whilst the oil will be little heated, and the ice not thawed.

A good class-experiment upon this subject, where it is necessary that effects should be seen at a distance, may be arranged as follows:—Let *A* (fig. 74) represent an inverted air-jar, which may be supported upon a ring-stand, filled up to the line *B* with cold water. *E* is a long-tubed air thermometer, fitted water-tight into the neck of the jar, the coloured liquid in which stands at about the level *E*, the bulb being surrounded by the cold water. A disc of thin cork nearly fitting *A* is then floated upon the water, and some hot water tinged blue or red is carefully poured up to the level, *c*, the cork disc (pre-



venting its mixture with the cold water beneath) may then be removed, and the hot coloured water remains floating upon the cold colourless water, and no effect is produced upon the thermometer. The syphon, *d*, is now carefully introduced, and the cold water gradually drawn off, so as to allow the hot coloured stratum to descend within a line of the bulb, but it still produces no effect till the hot water touches, and afterwards surrounds, the air-thermometer, when the liquid in its tube immediately descends from *e* into the cup.

These, and a number of similar facts and experiments, show that *water, and other liquids, are very imperfect conductors of heat*; and that fluids acquire and lose heat principally by the currents which have been described (pp. 140, 141), and which always take place in them when partially heated or cooled; the warmer parts ascending, and the colder descending. Whatever impedes these motions will proportionately interfere with the heating and cooling of the fluid. Hence viscid liquids, or those containing substances that mechanically thicken them, are more tardy in their reception and emission of heat than pure water: of this, thick soups afford a familiar example; they are a long time cooling.

The inference which has sometimes been drawn, that the state of liquidity prevents conduction, or the transfer of heat from particle to particle, is negatived, in regard to mercury at least, by substituting that metal for the cold water, in the apparatus, fig. 74; upon pouring hot water upon its surface, the thermometer is presently affected even through a considerable stratum of the fluid metal.

CONDUCTION BY GASES.—The experiments which have been made to determine the *conducting powers of gaseous bodies* are not very satisfactory in their results: and it has as yet scarcely been ascertained whether *air* is, or is not, properly speaking, a *conductor* of heat. A striking illustration of the non-conducting power of *steam* is afforded by carefully dropping a little water into a silver spoon or platinum crucible, heated nearly to redness; the water lies quietly upon the metal so long as it is prevented coming into perfect contact with it by the interposed layer of steam; but as soon as the crucible cools down, so as to admit the water to touch it, it instantly boils off. This explanation is however disallowed by M. Laurent. *Ann. de C. et P.*, lxii. 327.

When a heated body is suspended in the atmosphere, and freely exposed on all sides to air, it gradually parts with its excess of heat, so as to attain the temperature of the surrounding substances; but this cooling effect is produced by a variety of causes, independent of any real conducting power of the air. We have already alluded to the extreme facility with which currents are formed in air when heated substances are exposed to it: the warm air ascends, and a continual current is produced, which glides over the surface of the heated matter; thus, much heat is conveyed away by the establishment of currents, in consequence of change of density in the air. But heated bodies exposed to air also part with excess of temperature by *radiation*, a process continually going on from their surfaces, and which will presently require our minute attention. Upon the whole, it appears that *air is a very imperfect conductor of heat*.

REMARKS ON THE RELATIVE CONDUCTING POWERS OF BODIES.—It would

appear, from what has been stated, that those bodies which are the best conductors of heat, have the weakest attraction for it, and that bad conductors have the strongest attraction: the former, therefore, part with their heat more readily than the latter. Metals, which are excellent conductors, are easily heated, and as easily give out their heat. It is painful to touch metal heated to about 120° . Water scalds at 150° ; but air may be heated to 250° , or even 300° , without being painful to our organs of sensation. Sir F. Chantrey has a large stove, or oven, for drying the moulds employed in his bronze castings; a thermometer suspended in it generally stands at about 300° : the workmen enter and remain in it for some minutes without much inconvenience; and a person wholly unused to such high heats may walk into and out of it with impunity, though, to such, any attempt to remain generally occasions difficult breathing, and a painful sensation about the eyes, but the skin remains parched and dry. In subjecting ourselves to atmospheres thus highly heated, it is necessary carefully to avoid the contact of any good conductor of heat: if we touch a piece of metal, it would inevitably burn us; and a person once inadvertently entered with his spectacles on; which, being mounted in silver, presently burned the points of contact with his face.

The relative conducting powers of metal and wood are familiarly illustrated in the application of wooden handles to metallic vessels intended to contain hot liquids; or, sometimes, where the handle is required to be of metal, a thin piece of wood or ivory is interposed between it and the body of the vessel, by which all rapid communication of heat is effectually cut off.

We avail ourselves of the bad conducting power of brick and stone, in the construction of furnaces intended to retain their interior heat; but where the object is to communicate heat to the surrounding air, and not to retain it in the body of the furnace, they are made of cast or wrought iron, and the lining of brickwork is dispensed with, so that the heat may readily find its way outward.

A remarkable instance of the bad conducting powers of the earthy bodies constituting volcanic ashes is cited by Mr. Lyell, (*Principles of Geology*), in the preservation of a glacier near the summit of Etna, in consequence of its having been covered by volcanic dust, over which a current of lava afterwards flowed. He supposes that at the commencement of the eruption a deep mass of drift snow had been covered by volcanic sand showered down upon it before the descent of the lava. "A dense stratum of this fine dust," he says, "mixed with scorïe is well known to be an extremely bad conductor of heat, and the shepherds in the higher regions of Etna are accustomed to provide water for their flocks during summer, by strewing a layer of volcanic sand a few inches thick over the snow, which effectually prevents the heat of the sun from penetrating. Suppose the mass of snow to have been preserved from liquifaction until the lower part of the lava had consolidated, we may then readily conceive that a glacier thus protected, at the height of 10,000 feet above the level of the sea, would endure as long as the snows of Mont Blanc, unless melted by volcanic heat from below."

Charcoal is among the very worst conductors of heat; and there is a

well-known experiment which illustrates this, consisting in placing a tea-kettle of boiling water just taken from the fire, upon the palm of the hand: it is, of course, essential to its success that the bottom of the kettle should be well covered with soot, which is a porous form of charcoal, and effectually prevents the transmission of heat from the water within to the hand. So also when the palm of the hand is covered by a layer of dry sand, or of fine asbestos, a red-hot iron ball may be placed upon it with impunity.

The comparative conducting power of wood and metal is also well illustrated by the following experiment: take a smooth round bar of brass, or other *metal*, about an inch in diameter, and ten or twelve in length, and stretch a strip of writing-paper tightly over a part of it, to which apply the flame of a candle or spirit lamp, and it will be found impossible to burn or even singe the paper; for the heat passes through it to the metal, and is conducted away so rapidly, that its accumulation, or the temperature required to burn the paper, cannot be attained. If we now substitute a *wooden* bar of the same dimensions as the metallic one, stretch the paper over it, and hold it in the flame, the paper will presently singe and char, and the wood beneath will be inflamed, in consequence of its bad conducting power, which prevents the diffusion of the heat, and concentrates its effects upon the spot to which the flame is applied.

A stratum of confined air is an extremely bad conductor of heat: hence the advantage, in some instances, of double walls to furnaces, air being confined between them; and to icehouses, to exclude external heat; and of double windows to our apartments, to prevent the transmission of heat, and ingress of cold.

We have shown, that in air, the power of communicating heat is very feeble; its actual power of *abstracting* heat is also proportionably small: in the high northern latitudes, provided the air is tranquil, and there is no wind, a degree of cold may be sustained without injury, in which mercury freezes; but if, in this state of the atmosphere, *metallic* substances be touched, of the same low temperature, a sensation like that of burning is experienced, and the part becomes blistered.

We have above adverted to the effects of a high temperature upon the human body. The opposite effects of a very low temperature cannot be commanded artificially, and, therefore, opportunities seldom occur of witnessing them so as minutely to observe their consequences. Captain Parry and his associates, in their *Voyage for the Discovery of a North-west Passage*, frequently experienced a degree of atmospheric cold below the freezing of mercury. Under the date of Tuesday, the 15th of February, 1820, he says, "From four p.m., on the 14th, till half-past seven on the following morning, being an interval of fifteen hours and a half, during which time the weather was clear, and nearly calm, a thermometer, fixed on a pole between the ships and the shore, never rose above -54° , and was once, during that interval, namely, at six in the morning, as low as -55° . This low temperature might perhaps have continued much longer, but for a light breeze which sprung up from the northward, immediately on which the thermometer rose to -49° , and continued still to rise during the day, till, at midnight, it had reached

—34°. During the lowest temperature above mentioned, which was the most intense degree of cold marked by the spirit-thermometer during our stay in Winter Harbour, not the slightest inconvenience was suffered from exposure to the open air by a person well clothed, as long as the weather was perfectly calm; but in walking against a very light air or wind, a smarting sensation was experienced all over the face, accompanied by a pain in the middle of the forehead, which soon became rather severe. We amused ourselves in freezing some mercury during the continuance of the cold weather, and by beating it out on an anvil previously reduced to the temperature of the atmosphere; it did not appear to be very malleable when in this state, usually breaking after two or three blows of the hammer."

§ 7.—CAPACITIES FOR HEAT. SPECIFIC HEAT.

UNDER these terms we shall consider the relation of the *temperature* of bodies, whilst in the same state or form, to the *quantity of heat* contained in them. That the thermometer is an accurate measurer of temperature has been shown by Dr. Taylor's experiment already quoted, but, as was first proved by Dr. Black in his lectures at Glasgow, in 1762, it affords no correct insight into the *absolute quantity of heat necessary to produce a given temperature*: if, for instance, a pound of olive oil and a pound of water be brought from a cold into a warm room, from a temperature perhaps of 40° to a temperature of 70°, they will, it is true, gradually acquire the same temperature; and thermometers immersed in the respective liquids will gradually rise from 40° to 70°; but if we carefully watch the manner in which this rise of temperature is brought about, we shall find that the oil acquires the temperature of 70° more rapidly than the water; whence the inference, that the oil requires less heat to raise it from 40° to 70° than the water. Again, if we reverse the experiment, and transfer the two liquids from a warm to a cold room, it will then be observed that the oil cools more rapidly than the water: the fact is, that the quantity of heat required to raise water from 40° to 70° is much greater than that required to raise the oil a similar number of thermometric degrees, and consequently oil is more rapidly heated and cooled than a corresponding quantity of water. The following experiment proves this to be the case. A pound of *water* at 212° was surrounded, in a proper apparatus*, by ice, and the quantity of ice which was thawed by the heat given out by the water in cooling from 212° to 32°, was ascertained. A similar experiment was then made with the same weight of *oil*, and it was found that, in passing through the same range of temperature, it only thawed half as much ice as the water: although, therefore, the *temperatures* of the liquids were the same at the outset and conclusion of the experiment, the quantity of heat given out by the oil was only half that given out by the water; whence we infer that *bodies, though of the same temperature,*

* The instrument employed for this purpose was contrived by Lavoisier and Laplace, and is fully described in LAVOISIER'S *Elements of Chemistry*: they termed it a *Calorimeter*. Its inaccuracy, resulting from the difficulty of separating the water from the ice, has been shown by Wedgwood.—*Phil. Trans.*, vol. LXXIV.

do not contain the same quantity of heat, some requiring more, and some less heat, to raise them to a given thermometric point. The quantity of heat thus required is called the *specific heat* of the body; and if, in reference to the above statement, we call the specific heat of water 100, that of oil will only be 50; or, in other words, water has twice the *capacity for heat* that oil has.

It has been stated that equal quantities of the same fluid, at different temperatures, give the arithmetical mean, on mixture. Equal measures, for instance, of water at 70° , and of water at 130° , will give the mean temperature of 100° ; that is, the hot water loses 30° , and the cooler water gains 30° . But if equal measures of water at 70° , and of mercury at 130° be mixed, the resulting temperature will not be the mean, or 100° , but only 90° . Here, therefore, the mercury loses 40° , while the water only gains 20° ; hence the inference, that the quantity of heat required to raise a given measure of mercury 100° , will only raise the same measure of water 50° : that is, (speaking here of equal bulks, and not, as in regard to the oil, of equal *weights*;) the capacity of mercury for heat is only = half that of water. But the capacities of bodies for heat are most conveniently referred to equal weights rather than measures; and if we thus compare water with mercury, it will be found that a pound of water absorbs thirty times more heat than the same weight of mercury; viewed, therefore, in this way, the capacity of water for heat is to that of mercury as 30 to 1, or as 1000 to 33, and we generally thus express the capacities of bodies for heat by a series of numbers, having this reference to water as = 1000, such numbers being their *specific heats*. Dulong and Petit have shown, as Dalton had previously anticipated, that the specific heat of bodies increases with their temperatures, so that it requires more heat to raise them a given number of degrees when they are at a high than when at a low temperature. The specific heat of iron, for instance, at different temperatures, was as follows:—

From 32° to 212°	0.1098
“ 32 to 392	0.1150
“ 32 to 572	0.1218
“ 32 to 662	0.1255

The same holds good in respect to other bodies, as shown in the following table:—

	Between 32° and 212°	Between 32° and 572°
Mercury	0.0330	0.0350
Zinc	0.0927	0.1015
Antimony	0.0507	0.0547
Silver	0.0557	0.0611
Copper	0.0949	0.1013
Platinum	0.0335	0.0355
Glass	0.1770	0.1900

Petit and Dulong's researches, however, render it probable that the *atoms* (or weights indicated by their equivalent numbers) of simple substances, all have the same capacities for heat; hence the specific heat of an elementary substance, multiplied into the weight of its prime equivalent, should always give the same product (*Ann. de Ch. et Phys.*, vol. x. 403).

This curious subject has lately been elaborately investigated by

Regnault, (*Ann. de Chim. et Phys.*, LXXIII. 1.) from whom I have abridged the following table, from which it will be observed that the products of his specific heats multiplied by their atomic weights do, in fact, only vary from about 38 to 42, hence the law of Dulong and Petit is verified, especially if allowance be made for errors in the determination of the specific heats, as well as in that of the equivalent numbers. The latter, in fact, are in some cases altered from those usually adopted, in order to adapt them to this law, which obviously furnishes an important test of their correctness. Most of the atomic weights in the table are the same as those employed by Berzelius, and agree upon the oxygen scale with ours upon the hydrogen scale; that, however, of silver, is only half, and that of uranium one-fourth, while the atomic weight of carbon is doubled: if the equivalent thus obtained for carbon be correct, carbonic acid, instead of being represented by $\text{Car.} + 2\text{O}$, would be $\text{Car.} + 4\text{O}$; the neutral carbonates as they now stand would thus become basic carbonates; and the bi-carbonates would stand as the neutral salts containing an atom of acid and an atom of base. Some of these considerations are important, as influencing our views of the atomic constitution of certain organic compounds.

	Specific Heat.	Atomic weight adopted by Regnault.	Product of the two.
Water	1.00		
Glass	0.19768		
Brass	0.09391		
Oil of Turpentine	0.42593		
Iron	0.11379	339.21	38.597
Zinc	0.09555	403.23	38.526
Copper	0.09515	395.70	37.849
Cadmium	0.05669	696.77	39.502
Silver	0.05701	675.80	38.527
Arsenic	0.08140	470.04	38.261
Lead	0.03140	1294.50	40.647
Bismuth	0.03084	1330.37	41.034
Antimony	0.05077	806.45	40.944
Tin	0.05623	735.29	41.345
Nickel	0.10863	369.68	40.160
Cobalt	0.10696	368.99	39.468
Platinum	0.03243	1233.50	39.993
Palladium	0.05927	665.90	39.468
Gold	0.03244	1243.01	40.328
Sulphur	0.20259	201.17	40.754
Selenium	0.0837	494.58	41.403
Tellurium	0.05155	801.76	41.549
Iodine	0.05412	789.75	42.703
Uranium	0.06190	677.84	41.960
Tungsten	0.03636	1183.00	43.002
Molybdenum	0.07218	598.52	43.163
Steel	0.11848	339.21	40.172
Charcoal	0.24111	152.88	36.873
Phosphorus	0.1887	196.14	37.024
Mercury	0.0332	1265.82	42.149

The specific heat of gaseous bodies has been examined by De La Roche and Berard (*Ann. de Chim.* LXXXV., or *Ann. of Philos.*, v. ii.); the following tables show their general results:—

	Equal volumes.	Equal weights.	Sp. gravity.
Air	1·0000	1·0000	1·0000
Hydrogen	0·9033	12·3401	0·0732
Carbonic acid . .	1·2583	0·8280	1·5196
Oxygen	0·9765	0·8848	1·1036
Nitrogen	1·0000	1·0318	0·9691
Nitrous oxide . .	1·3503	0·8878	1·5209
Olefiant gas . . .	1·5530	1·5763	0·9885
Carbonic oxide . .	1·0340	1·0804	0·9569

To reduce these numbers to the standard of water, three methods were employed; from which the numbers 0·2498, 0·2697, and 0·2813 were obtained for atmospheric air. They have taken 0·2669 as the mean, to which all the above results are referred, as follows:—

Water	1·0000	Nitrogen gas	0·2754
Air	0·2669	Nitrous oxide gas . .	0·2369
Hydrogen gas . . .	3·2936	Olefiant gas	0·4207
Carbonic acid gas .	0·2210	Carbonic oxide gas . .	0·2884
Oxygen gas	0·2361	Aqueous vapour . . .	0·8470

An extended table of specific heats may be consulted in Dr. THOMSON'S *Outline of the Sciences of Heat and Electricity*, 2nd edit.: but there can be little doubt that many of the hitherto received results are erroneous, as will be evident from the observations of Regnault, in the paper above quoted; and as he is pursuing his inquiries and extending them to gaseous bodies and to compounds, I have not thought it necessary to extend the above tables or to quote the inferences of De la Rive and Marcet (*Ann. de Ch. et Ph.*, xxxv. and xl.) or those of Avogadro and Neumann (*Ibid.* lv. and lvii.)

The capacity of bodies for heat is very materially affected by their *density*; whenever density is diminished, capacity for heat is increased, and *vice versâ*. Thus in regard to *solids*, if we suddenly compress a piece of metal, it becomes hot, because its capacity for heat is diminished; and, therefore, in its dense and compressed state, it contains less heat than it did before; this is seen in the process of coining, where the blank piece, in sustaining the sudden and violent pressure of the coining-press, becomes suddenly warm; and a piece of soft iron, upon being dexterously struck a few heavy blows with a hammer, becomes hot enough to inflame the sulphur of a match. A piece of Indian rubber, suddenly and forcibly drawn out, becomes warm in consequence of the extension, as may easily be perceived by applying it to the lip the moment it is stretched, that part being very susceptible of slight changes of temperature.

Similar changes of capacity for heat, attending change of density, are also perceived in *liquids*. When sulphuric acid is mixed with water, the relative density of the mixture is suddenly and greatly increased, and it becomes boiling hot. When alcohol and water are mixed, there is also an increase of density, and heat is evolved.

In *gases* we have a convenient opportunity of observing that, as on the one hand, condensation produces heat, so, on the other, rarefaction, or diminution of density, is attended by increased capacity for heat, or, in

other words, by the production of cold. Air, suddenly compressed by the piston of a syringe, evolves so much heat as to inflame combustibles exposed to it; but if we suspend a thermometer in the receiver of the air-pump, we shall find that, during exhaustion, the rarefaction or expansion which the air suffers, causes a diminution of several degrees of temperature; and this is one reason why the air in the higher regions is so much cooler than that below. As it ascends from the earth it expands; and in expanding, its capacity for heat is increased: it therefore cools itself, as well as the surrounding bodies. The Andes, placed almost under the line, rise in the midst of burning sands; about the middle height is a pleasant and mild climate; the summits are covered with unchanging snows; and these ranges of temperature are always distinct. The hot winds from below, if they ascend, become cooled in consequence of expansion; and the cold air, if by any force of the blast it is driven downwards, is condensed and rendered warmer as it descends.

When hot steam suddenly issues, under great pressure, from a small aperture into the atmosphere, its instantaneous expansion so far cools it, that, instead of scalding the hand held in it, as is the case with ordinary steam, it scarcely feels warm.

Another case in point is furnished by the Fountain of Hiero, as it is called, at Schemnitz, in Hungary. A part of the machinery for working these mines is a perpendicular column of water, 260 feet high, which presses upon a quantity of air enclosed in a tight reservoir: the air is consequently condensed to an enormous degree by this height of water, which is equal to between eight and nine atmospheres; and when a pipe communicating with this reservoir of condensed air is suddenly opened, it rushes out with extreme velocity, instantly expands, and in so doing it absorbs so much heat as to precipitate the moisture it contains in a shower of snow, which may readily be gathered on a hat held in the blast. The force of this is so great, that the workman who holds the hat is obliged to lean his back against the wall, to retain it in its position.

If the blast from an air-gun be directed upon a delicate thermometer, it sinks it a few degrees, from the cold produced by the sudden expansion of the air.

§ 8.—EFFECTS OF HEAT IN CHANGING THE FORM OF BODIES.

LATENT HEAT.

HAVING described the phenomena attendant upon the expansion of bodies by heat, and its propagation through liquids and gases by change of density, and through solids by their convective or conducting powers, we may now proceed to an important part of the history of this power of matter, namely, to *its effects upon the forms or states of bodies*.

When *solids* are exposed to a certain degree of heat, they change their state, and are converted into *liquids*; and *liquids*, under the same circumstances, are changed into *vapours* or *elastic fluids*: these again, by the loss of heat, revert to the liquid state; and liquids, by due degrees of cold, are solidified*. *Ice, water, and steam* are familiar instances of these

* It is probable that all substances are susceptible of these changes; though, on the one hand, the temperature required for the liquifaction and evaporation of

three states of matter, and the phenomena attendant on their production may be discussed under the heads *Liquifaction* and *Vaporization*.

§ 9.—LIQUIFACTION.

ONE important fact respecting the conversion of ice into water has already been mentioned, in describing the method of graduating thermometers (page 148), namely, that, during the progress of thawing, the ice and the water always maintain an uniform temperature, which is equal to 32° of Fahrenheit's scale. Suppose, for instance, that we bring some pounded ice from a very cold place (say of the temperature of 0°) into a room of the temperature of 60° , the ice, of course, soon begins to liquify, and a thermometer plunged into it rises from 0° to 32° ; but there it remains *stationary* until the whole of the ice has melted: the water thus formed, then gradually rises to 60° , which is the temperature of the surrounding air. Now it is obvious, that during the whole process of thawing under the circumstances above described, heat must be entering the ice, but its effect is, not to elevate its temperature, but to melt it: the heat apparently combines with the ice, to constitute water, but it does not affect the thermometer.

To heat thus united with bodies, Dr. Black gave the name of *latent* or *combined heat*; and he instituted a number of elegant experiments upon the subject of liquifaction and congelation, one or two of which may be here detailed: they are at once simple and satisfactory.

Two similar glass globes were filled, the one with five ounces of water, which was afterwards frozen, and the other with water cooled down to 33° . That which contained the ice was allowed to remain in a warmer air, till the ice began to melt, at which time its temperature was 32° . The two vessels were then suspended in the middle of a large room without a fire, or any notable draught of air, and of the temperature of 47° . The vessels, therefore, were under similar circumstances of temperature within and without, and with similar contents, except that the one contained *ice*, and the other *water*. The progress of heating was then noted. In that which held the water, the thermometer rose in *half an hour* to 40° ; but, in the other, it took no less than *ten hours and a half* before all the ice was melted, and the contents had reached 40° . Consequently, the rate of heating was *twenty-one times slower* in the ice-vessel than in that which held the cold water; but the actual heat received by the former was obviously nearly uniform the whole time; and, therefore, it required about twenty-one times as much heat to bring ice to the state of water, and to raise it to 40° , as to raise ice-cold water to the same point. Or, to express it by another form: if the water had continued to receive as great an influx of heat as the ice during the whole twenty-one half hours, its temperature would, of course, have been raised twenty-one times as much as during the single half hour; and, as this was 7° , the whole would have been twenty-one times 7° , or 147° . The difference between the gain of

some solids is extremely high; and on the other, the temperature required for the reduction of many gases to the liquid state unattainably low. Fusion is sometimes preceded by a softening of texture so as to admit of adhesion by *welding*, as in

porcelain, glass, iron, and platinum: and certain solids which are very volatile rise in vapour before fusion; in order to liquify them, they require to be heated under pressure.

temperature in the ice and the water, with equal accessions of heat, is therefore about 140° ; and thus 140° is the expression of that quantity of thermometric heat or temperature, which disappears, or is rendered latent by the separate operation of the liquifaction of ice; the actual quantities of matter in the comparison being equal. BLACK'S *Lectures*, and AIKIN'S *Dictionary*, Art. CALORIC.

The conclusions drawn from the preceding experiment on the *slow* thawing of ice, were verified and confirmed by melting it *rapidly* by mixture with hot water. Thus, if we take any quantity of finely-pounded ice, or of snow, at the temperature of 32° , and mix it with an equal weight of hot water, at the temperature of 172° , the snow melts, and the temperature of the resulting water is only 32° . Here, therefore, the water suddenly loses 140° of heat, while the temperature of the snow remains as at the outset of the experiment. So that 140° of heat have disappeared; they have combined with the snow; and their effect has been, *not to raise its thermometric temperature, but to convert it into water*. Ice, therefore, when it is converted into water, absorbs and combines with a certain proportion of *sensible* heat, and renders it *latent*. The exact number of thermometric degrees of heat which disappear during the liquifaction of ice have been somewhat differently estimated by different experimentalists. The mean of the whole is about 140° , which also is Dr. Black's inference.

From the preceding experiments we deduce this important general law—that in all cases of liquifaction, a quantity of heat not indicated by, or sensible to, the thermometer, is absorbed or disappears; and that this heat is withdrawn from the surrounding bodies, leaving them comparatively cold.

The cases which we have cited are those of liquifaction at comparatively low temperatures, and relate to ice and water; but the same laws are observed in all other cases, and where the temperatures are comparatively high: to these the term *fusion* is generally applied: spermaceti, for instance, fuses at 112° , and retains that temperature during its fusion, so long as any portion remains unmelted: when the whole is liquid, and not till then, its temperature may be elevated above the fusing-point. Again, a ladleful of lead cannot be heated red-hot till all the metal is melted; and a quantity of red-hot melted lead is instantly cooled down to its point of fusion (which is about 612°) by the addition of a piece of solid lead.

That the heat which becomes insensible, or latent, during the liquifaction of ice and other solids, *remains* in the liquid, and is not altogether lost or destroyed, is shown by the circumstance of its being again emitted, or given out, during their congelation. If a vessel of warm water be exposed in a very cold atmosphere, the temperature rapidly sinks to the freezing-point, and then it begins slowly to congeal: if kept in the same situation, heat is of course abstracted as before; but the thermometric heat remains stationary at about 32° , till the whole is frozen, after which the temperature of the ice begins again to sink.

Perhaps the result of this experiment is more explicitly stated as follows (THOMSON'S *Outline*, &c.):—If, when the thermometer is at 22° , we expose a vessel full of *water* at 52° to the open air, and beside it another vessel full of *brine*, at the same temperature, with thermometers in each, we shall find that both of them gradually lose heat, and are

cooled down to 32° . After this the brine (which does not freeze till cooled down to 4°) continues to cool without interruption, and gradually reaches 22° , the temperature of the air; but the pure water remains stationary at 32° : it freezes, indeed, but very slowly; and during the whole process its temperature is 32° . Now why should one liquid refuse, all of a sudden, to give out heat, and not the other? Is it not much more probable that the water, as it freezes, gradually gives out the heat which it had absorbed during its liquifaction, and that this evolution maintains the temperature of the water at 32° , notwithstanding what it parts with to the air during the whole process? It is easily shown that water, while congealing, is constantly imparting heat to the surrounding air; for a delicate thermometer suspended above it is constantly affected by an ascending stream of air less cold than the air around.

The following experiment also shows that this *evolution of heat* actually takes place *during congelation*. (Sir C. BLAGDEN, *Phil. Trans.*, 1798.) If, when the air is at 22° , we expose to it a covered glass of water, with a thermometer in it, the water, if kept quite still, may be gradually cooled down to 22° without freezing. It is, therefore, ten degrees below the freezing-point. If the water be now shaken, part of it instantly freezes, and the temperature of the whole rises to 32° ; so that the water acquires 10° of heat in an instant. Now, whence comes this heat? Is it not evident that it is derived from that part of the water which suddenly froze; and consequently, *that water, in the act of freezing, gives out heat?*

There are many instances of the sudden or rapid liquifaction of bodies, in which the absorption of heat, or production of cold, are more remarkable and striking than in the cases above detailed. When finely-powdered common salt, for instance, is mixed with pounded ice or snow, a *sudden liquifaction* of the solids ensues, and a proportionate *production of cold*; they immediately run down into brine, which does not freeze till reduced to near 0° ; and a thermometer plunged into the mixture sinks nearly to that point. We sometimes avail ourselves of this process, to remove hard trodden snow from the pavement in winter: it is soon liquified by sprinkling a little salt upon it, and the temperature of the air is seldom low enough to freeze the brine which is produced. Confectioners employ the mixture of ice and salt to freeze cream in the hot weather of summer; and the same system is conveniently resorted to whenever considerable cold is required. The production of cold by the liquifaction of metals, may be well shown by melting together 207 parts of lead, 118 of tin, and 284 of bismuth; these form on cooling a brittle alloy, which when reduced to powder and dissolved in 1617 parts of mercury at the temperature of 60° , produce a liquid amalgam the temperature of which falls to 14° .

In the case of the disappearance of heat caused by the sudden formation of *liquid brine* from its *solid* constituents, the bodies being already cooled to 32° , the thermometer sinks about 30° , or to 0° . It was once supposed that this was the lowest temperature that could be artificially commanded; and hence, probably, our thermometric scale sets out with it: but we now know that, by careful management, the mixture of certain materials will afford a much more intense cold. Among the

most effective of these is the mixture of snow and the salt called *chloride of calcium* or *muriate of lime*: the snow should be taken in its light flocculent state, as it falls in a very cold winter's day; and the chloride, in fine powder, but not deprived of all its water of crystallization, should be mixed with it in the proportion of about three parts to two: the mixture should be made in earthen vessels, previously cooled, and in the lowest atmospheric temperature we can command; the thermometer will then sink from 32° , to between 40° and 50° below 0° , a temperature at which mercury freezes. By the successive application of freezing mixtures in a proper apparatus, Mr. Walker succeeded in sinking the spirit-thermometer to -91° ; a temperature at which all liquids, with the exception of pure alcohol, are converted into the solid form. The following table shows some of the most useful of these freezing mixtures, and the temperatures which result from their careful application. (*Phil. Trans.*, 1795 and 1801.)

Mixtures.		Thermometer sinks.
	Parts.	
Muriate of ammonia	. 5	From 50° to 10° .
Nitre 5	
Water 16	
Nitrate of ammonia	. 1	From 50° to 4° .
Water 1	
Sulphate of soda 5	From 50° to 3° .
Diluted sulphuric acid 4	
Snow 1	From 32° to 0° .
Common salt 1	
Muriate of lime 3	From 32° to -50° .
Snow 2	
Snow 2	From -10° to -56° .
Diluted sulphuric acid 1	
Diluted nitric acid 1	
Snow or pounded ice 12	From 18° to -25° .
Common salt 5	
Nitrate of ammonia 5	
Snow 1	From -40° to -73° .
Muriate of lime 3	
Diluted sulphuric acid 10	From -68° to -91° .
Snow 8	

Whenever ice can be procured, its mixture with common salt furnishes the cheapest and most effectual freezing mixture; but when it cannot be obtained, we often conveniently avail ourselves of the two first saline combinations in the preceding table: either the mixture of hydrochlorate of ammonia and nitre, or of nitrate of ammonia and water, may be used, and the salts again be obtained by evaporation. In employing them to cool a bottle of champagne, for instance, a vessel should be selected a little larger, and nearly as tall as the bottle; it should then be filled with the coldest pump-water that can be procured, and the bottle placed in it: about four ounces of the salt in fine powder should be sprinkled upon the

shoulder of the bottle, so as, gradually dissolving, to fall or run down its sides; as the salt dissolves, the bottle should be gently turned in the mixture, and kept in it till an immersed thermometer tells us that the temperature is rising, which will be in about twenty minutes or half an hour. A table of the cold produced by dissolving sulphate of soda in dilute sulphuric acid, by Professor BISCHOF of Bonn, will be found in Dr. THOMSON'S *Outline of the Sciences of Heat and Electricity*. "A very convenient process for freezing a little water without the use of ice is to drench finely-powdered (crystals of) sulphate of soda with the undiluted hydrochloric acid of the shops. The salt dissolves to a greater extent in this acid than in water, and the temperature may sink from 50° to 0° . The vessel in which the mixture is made becomes covered with hoar-frost, and water in a tube immersed in the mixture is speedily frozen."—(GRAHAM.)

As liquifaction is to surrounding bodies a *cooling* process, and as sudden liquifaction produces sudden cold, so solidification or congelation is to surrounding substances a *heating* process; and when it takes place suddenly, a proportionably sudden elevation of temperature is the consequence. In the experiment described in page 111, a solution of Glauber's salt is made suddenly to crystallize; and if the hand be applied to the flask, it will be found to become sensibly warm. In this case the heat evolved is chiefly referable to the water, which solidifies and constitutes the water of crystallization of that portion of the salt which separates in crystals; when alcohol is added to a saturated solution of sulphate of potassa, the salt is precipitated in the solid form, and the mixture becomes warm. When water is poured upon quick-lime, a sudden solidification of a large portion of water is effected in consequence of its attraction for the lime, which crumbles down into a dry white powder, and a great evolution of heat ensues, as we see by the steam which makes its escape in the ordinary operation of slaking lime. When water is poured upon sulphate of copper or sulphate of magnesia, previously deprived by heat of their water of crystallization, much heat is evolved in consequence of their resuming it: in this case also the water suddenly passes from the liquid to the solid state.

From the view, then, which we have taken of the constitution of *liquids*, it is obvious that they *may be considered as combinations of solids with heat*; that, consequently, when they revert to the solid state, they give out their *heat of fluidity*, which, previously *latent*, or *insensible* to the thermometer, now becomes *sensible*, in consequence of the change of state: on the other hand, when solids are converted into liquids, they absorb or combine with that portion of heat which is requisite to their respective fluidities.

Thus, the *heat of fluidity* or *latent heat* of water is 140° , and that of the following substances in their liquid state has been determined by Irvine, namely, sulphur 144° , spermaceti 145° , lead 162° , wax 175° , zinc 493° , tin 500° , bismuth 550° .

We may conclude this part of our subject with the following table, by Dr. Ure, showing the freezing and melting points, as they are called, of different liquids and solids; that is, the temperatures at which the former congeal, and the latter liquify.

Sulphuric ether					-46°
Liquid ammonia					-46
Nitric acid, spec. grav.	1.424				-45.5
Sulphuric acid, spec. grav.	1.6415				-45
Mercury					-39
Nitric acid, spec. grav.	1.407				-30.1
Sulphuric acid	1.8064				-26
Nitric acid	1.3880				-18
Ditto	1.2583				-17.7
Ditto	1.3290				-2.4
Brandy					-7.0
Sulphuric acid	1.8376				+1
Pure prussic acid					4 to 5
Common salt	25	+	water 75		4
Ditto	22.2	+	" 77.8		7.2
Sal ammoniac	20	+	" 80		8
Common salt	20	+	" 80		9.5
Ditto	16.1	+	" 83.9		13.5
Oil of turpentine					14
Strong wines					20
Rochelle salt	50	+	water 50		21
Common salt	10	+	" 90		21.5
Oil of bergamot					23
Blood					25
Common salt	6.25	+	water 93.75		25.5
Epsom salts	41.6	+	" 58.4		25.5
Nitre	12.5	+	" 87.5		26
Common salt	4.16	+	" 95.84		27.5
Copperas	41.6	+	" 58.4	+	28
Vinegar					28
Sulphate of zinc	53.3	+	water 46.7		28.6
Milk					30
Water					32
Olive oil					36
Sulphur and phosphorus, equal parts					40
Sulphuric acid, spec. grav.	1.741				42
Ditto	1.780				46
Oil of anise					50
Concentrated acetic acid					50
Tallow, (Dr. Thomson)					92
Phosphorus					108
Stearin from hog's lard					109
Spermaceti					112
Tallow (Nicholson)					127
Margaric acid					134
Potassium					136.4
Yellow wax					142
Ditto					149
White wax					155
Sodium					194
Sulphur, Dr. Thomson					218
Ditto Dr. Hope					234
Tin					442
Bismuth					476
Lead					612
Zinc, by Sir H. Davy					680
Ditto, Brongniart					698
Antimony					809

The solidifying temperature of the bodies above tallow, in the table, is usually called their *freezing* or *congealing point*; and of tallow and the bodies below it, the *fusing* or *melting point*.

The congealing points of the following metals are from Professor Daniell.

Mercury	- 39°	Zinc	773°
Potassium	+ 136	Silver	1873
Sodium	194	Copper	1996
Tin	442	Gold	2016
Bismuth	476	Cast Iron	2786
Lead	612	Pure Iron } above	3280
		Platinum }	

§ 10.—VAPORIZATION.

WE may now proceed to examine *the effects of heat upon liquids*. When liquids are heated, they are converted with more or less facility into invisible elastic fluids, or *vapours*. When water is heated in open vessels, its temperature gradually rises, and vapour is seen to form on its surface, which increases till the thermometer rises to about 212°, which is called the *boiling-point* of water: it is then violently agitated, and gradually disappears in the form of *steam*: but, although the source of heat is continued, the temperature of the water remains stationary, and both it, and the steam, continue at 212°. There are, therefore, in this simple operation, two leading circumstances to be attended to, namely, the degree of expansion which the water suffers by conversion into vapour; and the cause of that uniformity of temperature to which we have adverted, and which has been above noticed as furnishing one of the fixed points for thermometric graduation.

In regard to the *bulk* of steam formed by a given bulk of water, it appears, from the experiments of Gay Lussac, that a cubic foot of water is convertible into 1689 cubic feet of steam, at the temperature of 212° (the barometer standing at 29·9 inches). Mr. Watt conceived the bulk of steam to be about 1800 times that of the water; and others have far exceeded even Watt's estimate: we may, however, adopt that of Gay Lussac as the most accurate. Other liquids form different volumes of vapour; alcohol, for instance, gives 488 times its volume, ether about 212, and oil of turpentine 192, each at the temperature of 212°. It is obvious, therefore, that these vapours will differ materially in their respective densities. Steam is lighter than air, at the same temperature and pressure, in the proportion of about 10 to 16; the density of steam to that of air being as 625 to 1000. On the contrary, the vapours of alcohol, ether, and oil of turpentine are much heavier than air, the specific gravity of the first being 1·60, that of the second 2·58, and of the third 5·01, in reference to air as unity.

It has already been stated that the expansion of vapours by heat, and their contraction by cold, follows the same general law as that of gases, so long as the quantity of vapour continues the same; but if the vapour be in contact of the liquid producing it, then the increase of temperature will form a fresh portion of vapour, and the dilatation will proportionately exceed 1·480th of the whole bulk for each degree; so also will the contraction of a vapour on cooling deviate from the above law, whenever any portion reverts to the liquid state. Under varying pressure, the volume of vapour varies according to the same law as that of air, so long as the state of vapour is preserved.

Steam is an invisible elastic fluid like common air, and possessed of similar mechanical properties. We are, it is true, in the habit of associating a smoky appearance with steam, because we generally observe it when it is beginning to be condensed; as when it escapes, for instance, from the spout of a tea-kettle; but, when perfectly formed, it is quite invisible, as may be shown by boiling water in a flask, when perfect transparency will exist in the upper part of the vessel which is filled with the hot vapour; and it only becomes visible when it escapes into the air, and suffers incipient condensation.

The same general fact, in regard to the visibility of vapour, is shown by the production of *fogs*, which are occasioned by the mixture of warm with cold air; the general depression of temperature thus produced, rendering the aqueous vapour visible, in consequence of its partial condensation. This *partial* condensation does not amount to the actual precipitation of water, or *rain*; but consists of a multitude of thin *vesicles*; and hence the appearance is often called *vesicular vapour*: it constitutes clouds, mist, dew, and fogs. *Clouds*, therefore, are formed, whenever two masses of air, of different temperatures, and each saturated with moisture, meet and mix together; but what it is that subsequently causes the condensation of the vesicular vapour, and its precipitation in the form of rain, is not exactly known*.

Steam, as we have said, is produced by heating water to 212° under common barometrical pressure, the thermometer remaining fixed at that point, which is, therefore, called the *boiling-point* of water. *But this point, or temperature, varies with, and is immediately dependent upon, the pressure to which the surface of the water is exposed*; it is also, to a small extent, affected by the nature of the vessel containing the water. (GAY LUSSAC, *Ann de Chim. et Phys.*, vii., 307; *Quarterly Journal*, v., 361.) Thus in a glass flask the boiling-point of water often rises to 214° or 216° ; and where the steam is irregularly formed, occasioning a bumping in the vessel, the boiling-point is proportionately high and irregular, but upon throwing in a few metallic filings, pieces of wire, or other finely-divided and insoluble materials, the generation of steam is facilitated, and the boiling-point falls to its standard. Dr. Bostock has observed an analogous effect in ether and alcohol (*Ann. of Phil. N. S.*, ix., 196). Ether, heated in a glass vessel, had its boiling-point lowered many degrees by introducing a few shavings of cedar; and alcohol of the specific gravity of .849 had its boiling-point reduced in the same way

* "A mist or cloud consists not of solid drops, but of a multitude of very thin vesicles of water, similar to soap-bubbles. If clouds and fogs consisted of *drops*, their precipitation would be rapid; for a drop whose diameter amounted to a thousandth part of an inch would acquire a velocity of nine or ten feet per second: whereas we see clouds hover at a small elevation for hours; and they are transported from the sea, lake, river, or marsh, from which they are raised, far into the country, or to the tops of the mountains, where the requisite supply of

moisture cannot be had in any other way. Saussure, while travelling in the Alps, happened to be enveloped in a mist which was almost stagnant. He was astonished at the size of the drops, as he thought them, and at seeing them float slowly past him without falling to the ground. Some of them were larger than the largest peas. Catching them in his hand he found them to be bladders, inconceivably thin. Indeed, the optical phenomena exhibited by clouds and mists show that they are of a vesicular structure."—THOMSON.

between 30° and 40° . It is stated by Mr. Scrimgeour, of Glasgow, that if oil be present with water the boiling-point is always raised a few degrees.

The influence of fluctuations in the barometer upon the boiling-point of water is shown in the following table:—

Barometrical pressure, in inches, of mercury.	Temperature at which water boils.
27.74	208 $^{\circ}$
28.29	209
28.84	210
29.41	211
29.80	212
30.60	213

Of course, therefore, we find considerable *diminution* in the boiling-point of water upon the summits of hills and mountains, and other elevated situations; and a very delicate thermometer indicates a lowering of the boiling-point even at the top of high buildings. The Rev. Mr. Wollaston has described the method of constructing a thermometer of extreme delicacy, applicable to these purposes (*Phil. Trans.*, 1817). Saussure found that, at the top of Mont Blanc, water boiled at 187° . It appears from the above table that for every inch of variation in the barometer, the boiling-point of water varies 1.76 degrees; consequently, every tenth of an inch that the barometer rises or falls, either elevates or depresses the boiling-point by 0.176 of a degree; even the ordinary changes, therefore, in the height of the barometer will materially affect the boiling-point. In this country the *mean height* of the barometer is a little short of 30 inches: it very rarely rises higher than 31 inches, or falls below 28.5; so that from this cause alone, there will be a variation in the boiling-point of water of between four and five degrees.

The following table shows the boiling-points (at mean pressure) of several liquids, but the details upon this subject will be found under the separate heads of the substances themselves:—

Hydrochloric ether	52 $^{\circ}$
Sulphuric ether	96
Bisulphuret of carbon	116
Ammonia (sp. gr. 0.945)	140
Acetic ether	160
Alcohol (sp. gr. 0.798)	173
Water	212
Nitric acid (sp. gr. 1.42)	248
Crystallized chloride of calcium	302
Oil of turpentine	314
Naphtha	320
Phosphorus	544
Sulphuric acid (sp. gr. 1.84)	620
Whale oil	630
Mercury	662

The boiling-point of various saline solutions is partly dependent upon the quantity and partly upon the nature of the salt dissolved, and the steam arising from them has the same temperature as that of the boiling solution. (Faraday and Gay Lussac, *Ann. of Phil. N. S.*, v., 75.) Mr. T. Griffiths has determined the boiling-points of a number of saturated

solutions of salts, of which a table is given in the *Quarterly Journal*, xviii., 90. The following are a few of the results:—

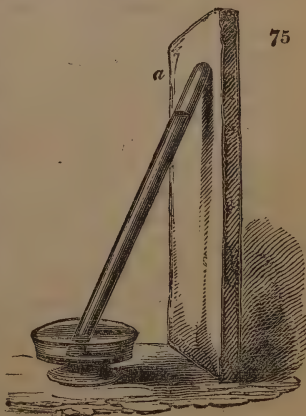
Name of salt.	Dry salt in 100 of solution.	Boiling point.	Name of salt.	Dry salt in 100 of solution.	Boiling point.
Acetate of soda . . .	60 . .	256°	Alum	52 . .	220°
Nitrate of soda . . .	60 . .	246	Chlorate of potash .	40 . .	218
Nitrate of potassa . .	74 . .	238	Sulphate of copper .	45 . .	216
Muriate of ammonia .	50 . .	236	Sulphate of iron . .	54 . .	216
Muriate of soda . . .	30 . .	224	Acetate of lead . . .	42 . .	215
Sulphate of magnesia .	57 . .	222	Sulphate of soda . .	31 . .	213

If, as has already been remarked, *pressure* be diminished by artificial methods, the temperature at which liquids boil will be proportionately lowered; and hence we often use the terms *boiling* and *ebullition* to signify the rapid conversion of water into vapour, *independent of the temperature at which it takes place*: using the term in this sense, we shall presently have occasion to point out a case of boiling at the freezing temperature.

The air-pump is a very useful instrument for showing the influence of diminished pressure upon boiling-points. If, for instance, we place a glass of water of the temperature of 90° or 100° under the receiver of the air-pump, and remove the air's pressure upon it, we shall observe that the water soon boils violently at that temperature; and would continue so to do, but that the space in the receiver becomes filled with an atmosphere of aqueous vapour, which, exerting its pressure upon the water, again prevents ebullition.

If we use liquids which, under ordinary circumstances, boil at temperatures below that of water, we shall find them boiling in *vacuo* at proportionately low degrees; this is the case with *ether* and with *alcohol*, which, under the above circumstances, readily boil at all common temperatures.

It may here be observed, that we apply the term *vapour* to all elastic fluids which are easily reconvertible into liquids: *steam* is easily converted into *water* by lowering its temperature a few degrees; and those liquids which have low boiling-points are especially convenient for illustrating these changes; such, for instance, as ether or alcohol; and as ether is only sparingly soluble in, and much lighter than water, it may be used in the following illustrative experiment. Nearly fill a glass tube about three feet long, and half an inch diameter, with water; then pour a little ether upon the surface of the water, and closing the open end of the tube carefully with the palm of the hand, invert it in a basin of water, as shown in fig. 75: the ether will rise through the water, and occupy the upper end of the tube, *a*, retaining, at common temperatures, its liquid state; but if we now pour a little hot water upon, or hold a heated iron near, the exterior of the tube, it presently causes the ether within to boil, and its vapour

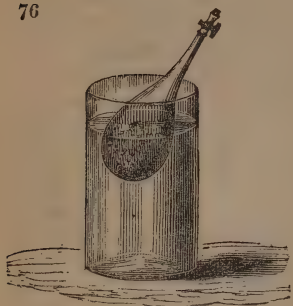


may thus be made to drive nearly the whole of the water out of the tube into the basin below: the ether retains this elastic or vaporous state, so long as its temperature is sufficiently high; that is, above 100° ; but if we now cool the tube, by suffering some cold water to dribble over it, the ethereal vapour returns to its liquid state, and floats upon the water as before. At temperatures above 212° , water would be in the same predicament as ether.

With regard to the bodies usually called *gases*, they are not thus easily condensable: a few of them become liquids when considerably cooled, and several others when subjected to great pressure; but at ordinary temperatures and pressures the gases are permanently elastic.

The following apparently paradoxical experiment illustrates the influence of diminished pressure in facilitating ebullition.

76



Insert a stop-cock securely into the neck of a Florence flask containing a little water, and heat it over a lamp till the water boils, and the steam escapes freely through the open stop-cock; then suddenly remove the lamp and close the cock; the water soon ceases to boil; but if the flask be now plunged into a vessel of cold water, as represented in fig. 76, ebullition instantly recommences, but it again ceases on holding the flask near the fire, or over the lamp. In this experiment

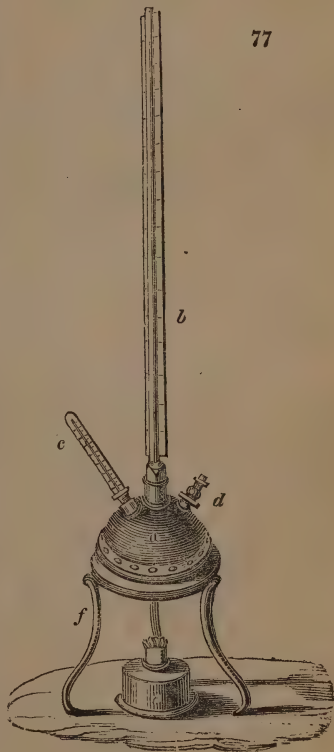
the air is driven out of the flask, and an atmosphere of steam included within it, which, upon immersion in cold water, is condensed, and a vacuum formed above the water, which, upon the principle already noticed, boils under the diminished pressure: the vacuum is kept up by the successive condensations of the portions of steam formed; but if the flask be removed from the cold medium, and especially if it be warmed, a new atmosphere of steam is formed, the pressure of which prevents ebullition.

Boiling in a more or less perfect vacuum is sometimes resorted to upon a large scale in the arts; and it has been successfully applied to the refining of sugar, the syrup being thus concentrated to the granulating point, without the risk of decomposing it. The same plan has been resorted to in the Pharmaceutical Laboratory, in the preparation of certain medicinal substances, the properties of which are easily impaired by heat. Mr. Barry has described a simple and effective apparatus for these purposes, in the *Medico-Chirurgical Transactions* (vol. x).

If we reverse the state of things just explained, and expose liquids to increased pressure, we proportionately elevate their boiling-points. Papin contrived an instrument for this purpose, which was called a *digestor*. It was a cylindrical copper vessel, having a lid very nicely fitted to it and secured by screws. If such a vessel be about half filled with water, with the lid closely secured, and then put upon the fire, steam is soon formed; but having no escape, it presses upon the water, and prevents the further formation of steam till the temperature of the water rises above the boiling-point. This heat being conveyed to the steam, it now receives

another portion of vapour without being condensed, and thus the *quantity* and *elasticity* of the steam are continually increasing with the temperature. Water has in this way been raised to the temperature of 419° , or even above it; for Muschenbroek asserts that he raised the temperature of the water high enough to melt tin, which requires a temperature of 440° . The powerful effects of high-pressure steam are illustrated upon a small scale by the little glass bubbles commonly called *candle or fire-crackers*; they are hermetically sealed, and contain a drop of water, which occasions them to burst with great violence, when sufficiently heated. But in speaking of the elastic force of steam it must be recollected that it does not in itself possess greater elasticity than air, so that vessels filled with steam only and containing no water in its liquid state, may be heated to any degree without more risk than if they only contained air.

The annexed is a good form of apparatus for illustrating, within certain limits, the influence of pressure upon the temperature of steam:—*a*, fig. 77, is a strong brass globe, composed of two hemispheres screwed together with flanches; a portion of quicksilver is introduced into it, and it is then about half filled with water: *b* is a barometer-tube passing through a steam-tight collar, and dipping into the quicksilver at the bottom of the globe: *c* is a thermometer graduated to about 400° , and also passing through an air-tight collar: *d* is a stop-cock, and *e* a large spirit-lamp. The whole is supported upon the brass frame and stand *f*. Upon applying heat to this vessel, the stop-cock being closed as soon as the water boils, it will be found that the temperature both of the water and of its vapour increases with the pressure, the extent of which is measured by the ascent of the mercury in the barometer-tube.



According to Southern, the temperature of steam under a pressure of two atmospheres is 250° , under that of four, 293° , and under that of eight, 344° . The results obtained by Dulong and Arago in reference to this question, are contained in the following table: they were obtained by experiment up to a pressure of twenty-five atmospheres, and at higher pressures by calculation. (*Quarterly Journal*, N. S. vii, p. 119.) See also Dr. Ure's table, *Phil. Trans.*, 1818.

Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.	Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.	Elasticity of the vapour, taking atmospheric press. as unity.	Temperature according to Fahrenheit.
1 ...	212	7 $\frac{1}{2}$...	336.86	19 ...	413.96
1 $\frac{1}{2}$...	233.96	8 ...	341.96	20 ...	418.46
2 ...	250.52	9 ...	350.78	21 ...	422.96
2 $\frac{1}{2}$...	263.84	10 ...	358.88	22 ...	427.28
3 ...	275.18	11 ...	367.34	23 ...	431.42
3 $\frac{1}{2}$...	285.08	12 ...	374.00	24 ...	435.56
4 ...	293.72	13 ...	380.66	25 ...	439.34
4 $\frac{1}{2}$...	301.28	14 ...	386.94	30 ...	457.16
5 ...	308.84	15 ...	392.86	35 ...	472.73
5 $\frac{1}{2}$...	314.24	16 ...	398.48	40 ...	486.59
6 ...	320.36	17 ...	403.82	45 ...	491.14
6 $\frac{1}{2}$...	326.26	18 ...	408.92	50 ...	510.60
7 ...	331.70				

The temperature of steam is always the same as that of the liquid producing it; hence the high temperature of steam generated under pressure: and as this elevation of temperature may be accurately regulated by the degree of pressure, *high-pressure steam* is often conveniently applied as a source of steady heat.

We are now to show, more particularly, that the production of vapour is in all cases attended by loss of sensible heat; and that, as in the case of *liquefaction*, heat disappears, to constitute the liquid, so, in all cases of *evaporation*, heat becomes, to a much greater extent, latent in the vapour.

The fact already adverted to, that we cannot, under ordinary circumstances, raise the temperature of water above 212°, although heat continues as before to flow into it, shows that the heat must be latent in the steam, the temperature of which does not exceed that of the water which produces it; and again, when water, as in the preceding experiment with the brass globe, is heated under pressure to a temperature above its ordinary boiling-point, the moment that that pressure is removed by suddenly opening the cock, a quantity of steam rushes out, and the remaining water has its temperature lowered to 212°. The quantity of water in this case, which constitutes the lost steam, is very small, yet it carries off the whole excess of heat from that remaining in the globe.

Dr. Black instituted some ingenious and simple experiments to determine the actual loss of heat during the conversion of water into steam. (BLACK'S *Lectures* and AIKIN'S *Dictionary*.) He heated water in a tin vessel up to its boiling-point, and noted the time required for the purpose. The same heat was then continued till the whole of the water was evaporated; and the time taken up by that process was also noted. Now, since, on the one hand, the accession of heat was constant, it was easily computed how high the temperature would have been, supposing the rise to have gone on above 212°, in the same ratio as below it; and, on the other, as the temperature of the steam was not raised, it was inferred that all the accession of heat from 212° was essential to the very state and constitution of steam at that temperature; this quantity was estimated at about 810°; that is to say, that the same quantity of heat which is required totally to evaporate boiling water at 212°, would be

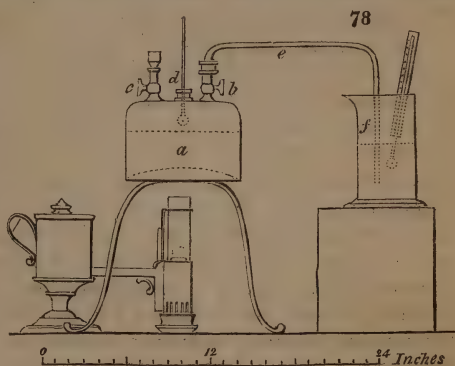
sufficient to raise the water 810° above the boiling-point, or to 1022° , if it had remained in the *liquid* state. Dr. Ure estimates the *latent heat* of steam at 1000° , and has given the following as the latent heats of other vapours.

Vapour of alcohol	457°	Vapour of nitric acid	550°
" ether	312	" liquid ammonia	866
" oil of turpentine	184	" vinegar	903

On the other hand, when steam is again condensed into water, it necessarily gives out the latent heat which was essential to its state of vapour, and which, being then set *free*, will raise the temperature of adjacent bodies as much more than an equal weight of boiling water would do, as the latent heat of the steam exceeds the sensible heat of the water*.

The small boiler, represented in fig. 78 may be conveniently employed in these experiments on the latent heat of steam. (HENRY'S *Elem. Chem.*)

For this purpose the tube *e* must be screwed on the stop-cock *b*, and immersed into the glass of water *f*. The cock *c* being closed, the steam arising from the boiling water *a*, will pass into the cold water *f*, the temperature of which will be much augmented by its condensation. Ascertain the increase of temperature and of weight, and the result will show how much a given weight of water has had its



temperature raised by a certain weight of condensed steam. To another quantity of water, of the same weight and temperature as that in the jar at the outset of the experiment, add a quantity of water at 212° , equal in weight to the condensed steam; it will be found, on comparing the resulting temperatures, that a given weight of steam has produced, by its condensation, a much greater elevation of temperature than the same quantity of boiling water. If, for instance, 100 gallons of water at 50° be mixed with 1 gallon at 212° , the temperature of the whole will be raised by about 1.5° . But, if a gallon of water be condensed from the

* It has sometimes been supposed from the low latent as well as sensible heat of the vapours of alcohol and ether, that they might be economically substituted for steam as sources of mechanical power, but as the cost in fuel would be

proportionate to the latent heat of equal volumes of their respective vapours it will be obvious from the following statement that if alcohol and ether could be procured as cheap as water, the latter would be most economical.

1 cubic foot of	Cubic feet of vapor.	Latent heat of equal volumes.
Water	= 1689	1000
Alcohol	= 488 : 457 :: 1689	1550
Ether	= 212 : 312 :: 1689	2500

state of *steam* in a still-tub containing 100 gallons of water, the water will in that case be raised 11° . A gallon of water, therefore, condensed from steam, raises the temperature of 100 gallons of cold water 9.5° more than the addition of a gallon of boiling water: consequently, if the heat imparted to 100 gallons of water by 10 pounds of steam could be condensed in 1 gallon of water, it would raise it to 950° ; and a gallon of water converted into steam of ordinary density, contains as much heat as would bring five and a half gallons of ice-cold water to the boiling-point. The quantity of ice which is melted by steam of mean density is seven and a half times the weight of the steam.

In breweries and other manufactories where large quantities of hot water are consumed, it is frequently heated by conveying steam into it, or by suffering steam pipes to traverse the vessels, or by employing double vessels. This method of warming water has also been advantageously applied to heating baths. Where a higher temperature than 212° is required, it is necessary to employ steam under adequate pressure. The heat given off by steam during its condensation, is also often applied to warming air, and is at once safe, salubrious, and economical.

Whatever may be the *density* of steam, the same weight contains the same quantity of heat, so that distillation or evaporation at low temperatures is not attended by any saving of fuel; the latent heat is increased in proportion as the sensible heat is diminished. (SHARPE, *Manchester Memoirs*, 2nd series, ii.) Mr. Daniell illustrates this principle as follows. "Let us imagine that in a cylinder furnished with a piston we have a certain quantity of steam, and that it is suddenly compressed by a stroke of the piston into half its bulk without being reduced to the liquid state: it would acquire double elasticity, and its temperature would be increased. If we either suppose the cylinder incapable of transmitting heat, or take the moment instantly following the compression, before any heat has had time to escape, it must be evident that the sensible and latent heat together before the compression are precisely equal to the sensible and latent heat after the compression; but in the dense steam the sensible heat is increased and the latent heat diminished by equal quantities. Reversing this imaginary experiment, if we suppose only half the cylinder to contain steam at 212° , and the piston to be suddenly raised so as to double its volume, the density will of course be reduced to half, and its temperature will fall, but its sensible and latent heat together will remain unchanged." Mr. Daniell quotes the following results of Clement and Desormes in reference to this subject.

A certain weight of steam at 212° condensed at 32° , gives out	}	180° sensible heat.
		950 latent heat.
		<hr/> 1130
		<hr/>
The same weight at 250°	}	218 sensible.
		912 latent.
		<hr/> 1130
		<hr/>
The same weight at 100° . . .	}	68 sensible.
		1062 latent.
		<hr/> 1130
		<hr/>

The existence of vapours of great density under high pressures and temperatures has been shown by the experiments of M. Cagniard de la Tour. (*Ann. de Ch. et Phys.*, xxi. 127—178; *Quarterly Journal*, xv. 145.) Although pressure restrains the volatilization of a liquid, it occurred to him that there should be a limit beyond which liquids would notwithstanding be converted into vapour, provided sufficient space be allowed for its generation. A strong glass tube, two-fifths filled with alcohol, and hermetically sealed, was slowly and carefully heated; as the fluid dilated, its mobility increased, and when its volume was nearly doubled, it suddenly disappeared, and became a transparent vapour. The same results were obtained with naphtha and ether; the latter requiring less space than the former to be converted into vapour without breaking the tube, and naphtha less space than alcohol. The presence of atmospheric air in the tubes did not interfere with the results. The same experiment succeeded, though difficultly, with water, the tube containing only about one-fourth its volume. M. Cagniard de la Tour ascertained, by means of a mercurial gage, the pressures of the above vapours. Alcohol, occupying in vapour a space little more than thrice its liquid volume, exerted a pressure = 119 atmospheres, and required for its production a temperature = 405° . Ether, under the same circumstances, exerted a pressure of 38 atmospheres at 320° . The temperature of the dense vapour of water was nearly that of melting zinc.

The same general laws which preside over the formation of steam at *high* temperatures influence its production at *low* temperatures: the constitution of vapour, therefore, is always the same. When water slowly evaporates under exposure to air, its vapour mixes with the surrounding atmosphere, and the process is usually called *spontaneous evaporation*; it takes place at all temperatures, and with a rapidity proportionate to the dryness of the air, and the velocity of the current passing over it: thus, in manufactories, where large quantities of liquids are to be evaporated, instead of heating them in the usual way, a current of hot air is made to pass over the surface of the fluid.

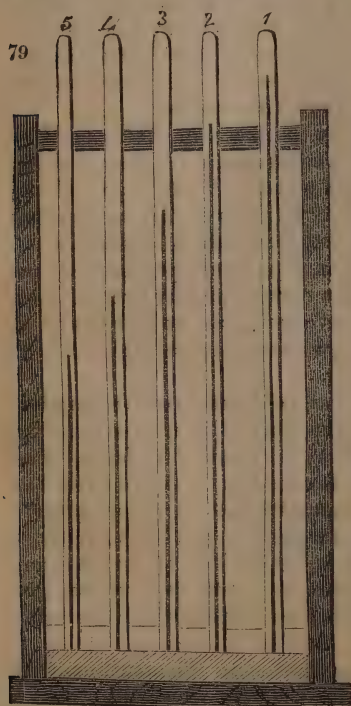
As, therefore, vapour slowly formed in cases of spontaneous evaporation, is similarly constituted to that produced by rapid ebullition, there being the same loss of *sensible heat* in the one case as in the other, it follows that the exhalation of humidity which is almost constantly going on from the earth's surface, must powerfully modify natural temperatures, and prevent accumulation of heat; the vapour forms mists and clouds, and when these are condensed into rain, their latent heat is again given out in the upper and cold regions. The conversion, therefore, of water into vapour, and the condensation of vapour in the form of dew and rain, is a process of the utmost importance, and tends considerably to the equalization of temperature over the globe. Dalton has shown that the actual quantity of vapour which can exist in any given space, entirely depends upon temperature. Thus, if some water be put into a dry flask, at 32° , very little vapour will be formed; it will contain more at 50° , and yet more at 70° . But if, being at 70° , the temperature be lowered to 32° , vapour will be condensed, and the portion retained will not exceed that originally taken up at 32° . The actual result of these experiments is the same when the flask is empty as when it contains air, but in the former case the evapora-

tion is most rapid, for the air affords some mechanical resistance to the distribution of the vapour.

The following table shows the elastic force and the weight of aqueous vapour at different temperatures:

Temp.	Tension in inches of Mercury.	Weight of a cubic foot.
32°	0·216	2·53 grains.
40	0·280	3·23
50	0·400	4·53
60	0·560	6·22
70	0·770	8·39
80	1·060	11·33
90	1·430	15·00
212	30·000	257·22

The relative volatility of bodies and the elastic force of their respective vapours may be estimated by their effects upon the column of mercury in the barometer tube. Thus, if we range five barometers side by side, one of which may serve as a standard, and then throw up a little water into



the second, alcohol into the third, ether into the fourth, and sulphuret of carbon into the fifth, each column will be depressed in proportion to the elastic force of the respective vapours. If the whole space above the mercury in each tube be equally heated, the increase of tension with increase of temperature may be measured; but if the liquids only be heated, the tension will not increase, because the respective vapours will be condensed as soon as formed. 1, represents the standard barometer; 2, the depression by the vapour of water; 3, by alcohol; 4, by ether, and 5, by sulphuret of carbon.

When liquids are exposed to the atmosphere, evaporation is proportionate to the surface exposed, and is therefore greatly accelerated by increasing the surface, as by exposing them in very shallow vessels, or suffering them to trickle over solid bodies; it is also accelerated by agitating the superincumbent air, as in the case of a brisk wind, or by artificial means: when the air is tranquil, the vapour

rests upon the surface of the water, and it is the pressure of its own vapour on the surface of a liquid, and not that of the gaseous atmosphere, which stops the process. The following table, drawn up by Mr. Daniell from the experiments of Dr. Dalton, shows the force of vapour at different temperatures, and the rate of evaporation per minute from a circular sur-

face six inches diameter; the amounts of evaporation refer to dry air; if vapour be already present, as it always is in our atmosphere, the quantity of evaporation at any given temperature will be the quantity indicated in the table, *minus* the quantity already incumbent upon the water. (DANIELL, § 196.)

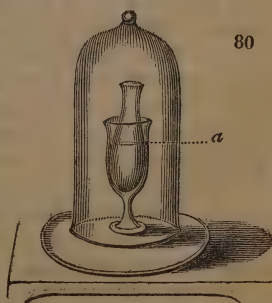
Temp.	Force in inches of Mercury.	Calm. grs.	Breeze.	High Wind.
212°	30·000 . . .	120·00 . . .	154·00 . . .	189·00
85	1·235 . . .	4·92 . . .	6·49 . . .	8·04
75	0·906 . . .	3·65 . . .	4·68 . . .	5·72
65	0·657 . . .	2·62 . . .	3·37 . . .	4·12
55	0·476 . . .	1·90 . . .	2·43 . . .	2·98
45	0·340 . . .	1·36 . . .	1·75 . . .	2·13
35	0·240 . . .	0·95 . . .	1·22 . . .	1·49
25	0·170 . . .	0·67 . . .	0·86 . . .	1·05

By inducing rapid evaporation, at common or low temperatures, we have it obviously in our power to produce considerable degrees of cold. If a wet cloth is spread out in a keen wind at a temperature a few degrees above freezing, the water, by its rapid evaporation, soon carries off so much heat as to freeze the remainder, making the cloth hard and stiff by the formation of ice within its pores.

There is no liquid better calculated for making experiments on the cold produced by spontaneous evaporation, than *sulphuric ether*; it is extremely vaporisable at ordinary temperatures, and if we pour a little of it into the palm of the hand, and blow gently upon its surface, we observe that, as it disappears in vapour, a very sensible degree of cold is produced.

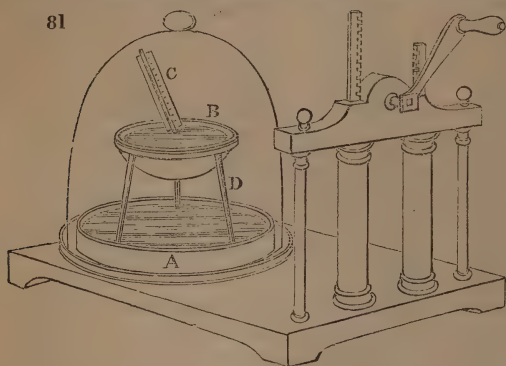
If we fold a strip of cambric round the bulb of a small thermometer and suffer ether to dribble over it from a dropping-bottle, at the same time accelerating the evaporation by blowing gently upon it with the mouth or a pair of bellows, we shall observe the mercury fall to several degrees below the freezing-point; and if we substitute for the thermometer a thin glass tube, containing a small quantity of cold water, a little dexterous management will enable us by the same means to freeze it.

This congelation of water by the evaporation of ether, furnishes, by the help of the air-pump, a very striking experiment. Provide a small thin glass flask, which fits tolerably close into a bell-shaped wine-glass, as represented by the annexed cut (fig. 80). Pour a little good ether into the flask, and some cold water into the wine-glass, so that each may stand at about the level *a*, and place the whole apparatus, thus arranged, under the receiver of an air-pump. During exhaustion, the ether will *boil*, that is, it will very rapidly pass off in the state of vapour. Now, the vapour of ether, like all others, requires *heat* for its formation, and this it takes from the surrounding bodies, and, among the rest, from the adjacent water, which soon *freezes* in consequence of the loss of that portion of heat which was essential to its fluidity, but which has been carried away and pumped out in the



ethereal vapour. It sometimes happens that the success of this experiment is prevented by the ether boiling over into the water, and so preventing its congelation; but this may be guarded against by putting a little bit of wood or paper into the ether, which causes it to boil regularly, and prevents sudden jets of vapour.

There is an experiment yet more illustrative of the absorption and disappearance of sensible heat during evaporation, which consists in freezing water by causing it rapidly to evaporate at low temperatures; it

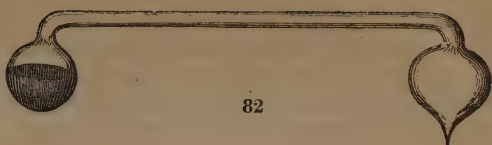


is performed as follows: upon the plate of a good air-pump place a flat shallow glass dish, A, about half-filled with sulphuric acid, and a little above it a tin or copper basin, B, three parts filled with water, with a small thermometer, c, immersed in it (fig. 81). This basin, which should be of the shape shown in the cut, may be conveniently

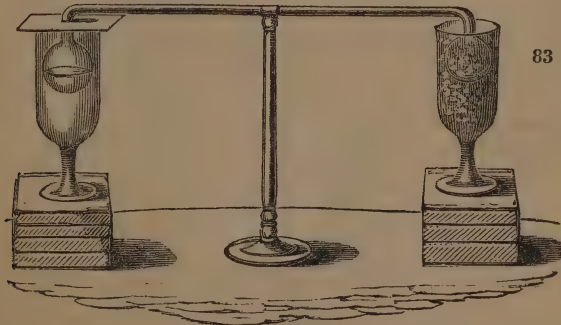
supported upon three glass legs, D, standing in the acid. Over the whole, place an air pump receiver, not larger than requisite, and proceed to withdraw the air. We first observe the escape of air from the water; the thermometer gradually sinks; the water then, in consequence of the rapidity of its evaporation, appears to boil; and if the whole apparatus is in good order, it freezes in the course of five or ten minutes. The use of the sulphuric acid is to absorb the aqueous vapour, which it does very energetically, and consequently occasions a constant fresh call upon the water for its formation. Now we have shown that *vapour cannot be produced without the absorption of heat*; and, in the case before us, the heat requisite to convert *one* part of the water into *vapour* is taken from the *other fluid portion*, which, thus losing the heat that constituted its fluidity, becomes solid, or freezes. There is another phenomenon often observable in this experiment, which is, that the temperature of the water falls several degrees below the freezing-point, before congelation takes place; but the moment that it freezes, it rises to 32° , in consequence of the escape of the residuary latent heat. Leslie, who contrived this process, proposed it as a means of procuring ice in hot climates, and suggested for the purpose, a large single air-pump, capable of exhausting six or eight receivers at a time. He has also shown, that parched oatmeal, and certain dried earthy substances, may be substituted, as absorbents, for the sulphuric acid; but they are far less effectual.

Dr. Wollaston's *cryophorus*, or ice-bearer, illustrates the same general facts, in a more simple manner than the preceding; it depends upon the same common principle, but the vacuum and the evaporation are brought about in a different way. It is a tube, having a bulb at each extremity, one of which is half filled with water, as represented in fig. 82; the interior of

the tube is perfectly deprived of air, by boiling the water in one of the bulbs till a jet of pure steam issues through a small opening left at the



bottom of the other, which is then sealed by fusion in the flame of a lamp the consequence is, that the water in the other bulb is greatly disposed to evaporate; but this evaporation can only proceed to a certain extent, because the pressure of vapour within the tube soon prevents its further progress. To get rid of this, to keep up the vacuum, and to occasion a constant demand upon the water for the fresh formation of vapour, the empty ball is plunged into a freezing mixture, which continually condenses the vapour within, and so accelerates the evaporation of the water in the other bulb, as to cause it ultimately to freeze. The success of this experiment, when it is attempted in a warm room, where there are several persons, is often frustrated by the rapid deposition of moisture, arising from the condensation of ærial vapour upon the water-bulb; an effect which may be prevented by protecting it from the free access of fresh portions of air, by immersion in a covered glass, as shown in the following sketch, fig. 83, which also represents the empty bulb surrounded by a freezing mixture of pounded ice and salt. The intermediate tube between the bulbs of the cryophorus may be of any length: about two feet is most convenient, for when longer it is very apt to be broken.



There are many cases in which we resort to accelerated evaporation, at common temperatures, as a source of cold, without, however, carrying it so far as to produce ice. The sprinkling of floors and pavements with water tends to cool them and the air, by its evaporation at summer temperatures: *wine-coolers* are porous earthen vessels, which are dipped into water, and, during exposure to air, become cooled by its escape from their surfaces in the form of vapour; and in some hot climates, porous bottles are filled with water, and suspended in a current of air; the water oozes to the surface, whence it is rapidly removed by evaporation, and cold is consequently produced.

It will be obvious, from the facts now adduced, that all *vapours* may be considered as combinations of solids or liquids with heat, and Mr.

Faraday's discoveries sanction us in regarding *gases* as similarly constituted; some of these are condensible by *cold*, others by *pressure*, into the liquid state: and we thus learn that they are merely the vapours of extremely volatile liquids, the boiling-points of which, under common atmospheric pressure, are, in many instances, lower than any natural temperatures. Under great pressure these gases may be coerced into the liquid state, and, upon its removal, they instantly reassume the gaseous form, some with explosion, and some with the appearance of brisk ebullition, and the production of intense cold.

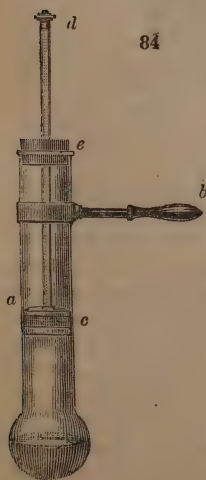
Mr. Faraday condensed the gases by exposing them to the pressure of their own atmospheres. He put the materials for producing them into a strong glass tube, a little bent in the middle, and hermetically sealed. When necessary, heat was applied, and when the pressure within became sufficient, the liquid made its appearance in the empty end of the tube, which was artificially cooled to assist in the condensation. In these experiments much danger is incurred from the bursting of the tubes: so that the operator should protect his face by a mask, and his hands by thick gloves. He succeeded in liquifying the following gases, which, as will be seen, require various degrees of pressure for the purpose.

	Pressure in Atmospheres.	Fahr.		Pressure in Atmospheres.	Fahr.
Sulphurous acid	2	at 45°	Sulphuretted hydrogen	17	at 50°
Chlorine	4	„ 60	Carbonic acid	36	„ 32
Cyanogen	4	„ 60	Muriatic acid	40	„ 50
Ammonia	6.5	„ 50	Nitrous oxide	50	„ 45

§ 11.—THEORY OF THE STEAM-ENGINE.

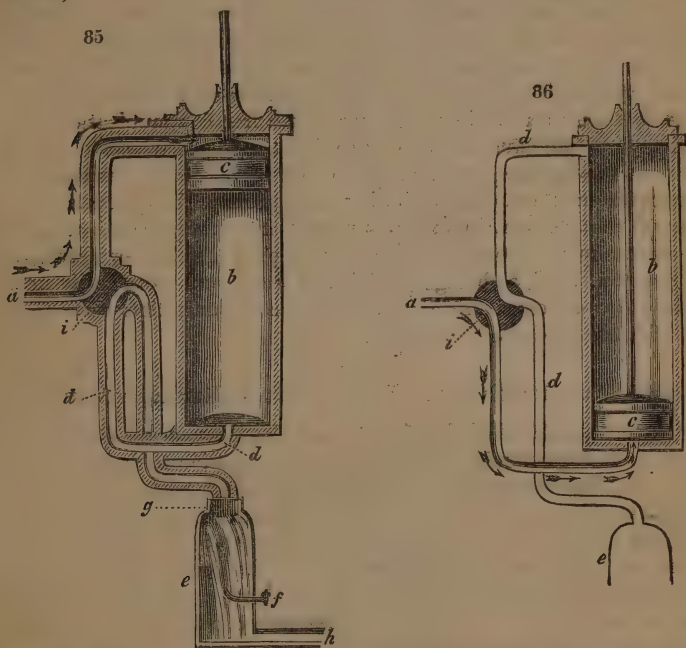
So many of the phenomena attendant on evaporation and liquifaction are illustrated by the action and principles of the *steam-engine*, that it may be worth while to refer to the construction and operation of that machine, as elucidating several points already adverted to.

The action of the steam-engine depends principally upon the two leading properties of steam which have been dwelt upon—namely, *its expansive force*, and *its easy condensation*. To take the most simple view of these as moving powers, let *a*, fig 84, represent a glass tube with a bulb at its lower end. It is held by a ring and handle *b*, and contains a piston *c*, which, as well as its rod, is perforated, and may be opened or closed by the screw at top *d*: it is kept central by passing through a slice of cork at *e*. When used, a little water is poured into the bulb, and carefully heated over a spirit-lamp; the aperture in the piston-rod being open, the air is thus expelled, and when steam freely follows it, the screw may be closed, when, on applying cold to the bulb, the included steam is condensed, and a vacuum formed, which causes the descent of the piston, in consequence of the air pressing upon it from above. On again holding the bulb over the lamp, steam is reproduced, and the piston again



forced up; and these alternate motions may be repeatedly performed by the alternate applications of heat and cold. This instrument gives a tolerably correct notion of the application of steam in the old engines, where it was employed conjointly with the air's pressure as a moving power.

In the most perfect construction of Watt's engine, steam is exclusively employed both for elevating and depressing the piston; and the following diagrams and description may perhaps enable the reader to understand the very ingenious method in which it is thus applied:—(See figs. 85 and 86.)



a is the *steam-pipe* issuing from the boiler, and so contrived as alternately to deliver steam into the *cylinder b*, above and below the piston *c*.

b is the main *cylinder* of the engine.

c is the *piston*, with the *piston-rod* passing through an air-tight collar at the top of the cylinder, which is commonly called the *stuffing-box*.

d is the *eduction-pipe*, by which the steam, having performed its duty in the cylinder, makes its escape into the *condenser*.

e is the *condenser*, immersed up to the level *g*, in a cistern of cold water.

f, the *injection-cock*, by which a small jet of cold water is admitted into the condenser.

h, a pipe communicating with a pump called the *air-pump*, by which the condensed steam and injection-water are continually pumped out of the condenser: it also pumps out the air, and keeps a constant vacuum in the cylinder and condenser.

i represents the moveable plug of a cock which has two passages, and which opens alternate communications with the steam-pipe and the eduction-pipe. In fig. 1, this plug is shown in the position which admits the steam to pass into the cylinder *above* the piston: in fig. 2, the plug has shifted its position, and now admits the steam to pass into the cylinder *below* the piston: in the former case the condenser is open to the space below the piston; in the latter, to the space above the piston.

Let us now suppose a vacuum to exist in the cylinder *b*; the steam passes through the pipe *a*, in the direction of the arrows (fig. 85), and entering the cylinder *above* the piston, immediately forces it *downwards*. The piston having reached the bottom of the cylinder, the plug of the cock *i* shifts its position, and is now as represented in fig. 86; the steam enters as before at *a*, and passes in the direction of the arrows to the *bottom* cylinder, so as to *elevate* the piston. It is obvious that this action could not take place unless the steam, by which it had previously been depressed, were removed; this therefore makes its escape by the *eduction-pipe d*, (fig. 86), and passes into the *condenser e*, where it reverts to the state of water, which is got rid of by the *air-pump* through the pipe *h* (fig. 85). The piston being now in the position represented in fig. 85, and the plug having again shifted its position, the steam enters *above* the piston as before, while the space *under* the piston has now a free communication with the condenser by the eduction-pipe *d*; so that the steam, which had first been active in raising the piston, is not in the way of its depression. I have here represented and described what may, perhaps, be called the simplest form of this engine, in order to render its *principle* as intelligible as diagrams admit. Instead of the four-way plug *i*, sliders or sliding-valves are generally used, as being less liable to wear, and more easily kept airtight; but in all cases the same alternate communication with the boiler and with the condenser is effected.

§ 12.—RADIANT MATTER. REFLECTION AND REFRACTION OF LIGHT.

OF the substances belonging to our globe, some are of so subtle a nature as to require minute and delicate investigation to demonstrate their existence; they can neither be confined nor submitted to the usual modes of examination, and are known only in their states of motion, as acting upon our senses, or as producing certain changes in the more gross forms of matter. They have been included under the general term of **RADIANT, IMPONDERABLE, or ETHEREAL MATTER**, which, as it produces different phenomena, must be considered as differing either in its nature or affections. Respecting the nature of these phenomena, two opinions have been entertained, and each ably supported. It has been supposed by Huygens, Euler, and Descartes, that they arise from vibrations of a rare elastic medium which fills space; while Newton has considered them as resulting from emanations of particles of matter. The former opinion has been ably advocated by Dr. Young, who has selected from Newton many passages favourable to the undulatory theory, and has shown that it explains phenomena not easily consistent with the theory of radiating particles. (Young's *Nat. Phil.*, ii., 631. See also Fresnel's *Exposition of the Undulatory Theory* in the first volumes of the *Quarterly Journal*, *N.S.*)

It may suffice here merely to advert to these opinions, without touching upon the reasoning by which they are respectively supported, and which has no immediate connexion with chemical science: there are, however, certain affections and effects of light, and of the heat that radiates from the sun, and from terrestrial bodies, which form an important part of chemical philosophy, and constitute one of the principal links by which it is connected with physical inquiries.

The phenomena of vision are produced either by bodies inherently luminous, such as the sun, the fixed stars, and incandescent substances; or they are referable to the reflection of light from the surfaces of bodies. It is thus that the objects around us are visible by reflecting the sun's rays in the day-time, but become lost in obscurity when that luminary sinks beneath the horizon. The manner in which the eye is affected by luminous bodies, shows that light is transmitted in *right lines*, and every right line drawn from a luminous body to the eye is termed a *ray of light*; and, as a congeries of rays possesses the same properties as the single ray, the same abstract term is frequently employed to designate the congeries, which is also called a *pencil* of rays.

The discoveries of Roemer, (*Phil. Trans.*, vol. xii.,) and of Bradley, (*Phil. Trans.*, vol. xxxv. and xlv.,) have shown that *the motion of light is progressive*, and that it is about eight minutes and thirteen seconds in passing from the sun to the earth, so that it may be considered as moving at the rate of 192,000 miles in a second; and, in the language of Herschel, (*Discourse on the Study of Natural Philosophy*, p. 23,) it performs the tour of the world "in about the same time that it requires to wink with our eyelids, and in much less than a swift runner occupies in taking a single stride." It is with extreme difficulty that we can conceive either emanations of matter or ethereal undulations to assume such extreme velocity, for, in the former case, how inconceivably minute must particles be, not only to impinge without injury upon terrestrial objects, but even to fall without pain upon our delicate sensual organs; and in the latter, how subtle and attenuated must be the medium by or through which the vibratory impulses are communicated.

We get some notion of *the velocity of light* by comparing it with the progress of *sound*, which moves at the rate of about 1000 feet in a second, or 760 miles in an hour; yet, its comparatively tardy progress is recognised, in observing the time that elapses between the flash and the report of a gun fired at a distance; the latter reaching the ear some time after the former comes to the eye; a period of nearly five seconds elapses when the gun is only a mile off, and we are thus enabled with some degree of accuracy to calculate the distance of luminous phenomena attended by sound; the varying time that elapses between seeing a flash of lightning and hearing the thunder is another familiar instance, and from it we infer the distance and course of the electric discharge.

Although, therefore, the sun is so far distant from the earth, that a cannon-ball, proceeding with its greatest speed, would be twenty years in reaching it*, and, that although almost a million times larger than the earth, its magnitude, as viewed from the earth, scarcely exceeds that of the moon, which is not much more than one-fourth the diameter of our globe, (the former 2160; the latter 8400 miles; the diameter of the sun being 882,000 miles,) yet, such is the velocity of light, that a flash of it from that luminary would be seen in little more than eight minutes after

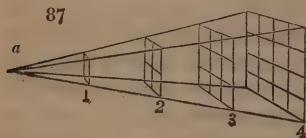
* "The earth, moving at the rate of nineteen miles in a second, would take two months to pass through a distance which a ray of light would dart over in eight minutes. The subsequent discovery of the aberration of light confirmed this astonishing result."—MRS. SOMERVILLE.

its emission; whereas, the sound evolved at the same time (supposing a medium like air capable of conveying sound between the sun and the earth, and the distance 95 millions of miles) would not reach us in less than 14 years and 87 days. It is evident, therefore, that certain astronomical phenomena are not visible upon the earth, till a certain time after their occurrence; and it was this observation, as applied to the eclipses of Jupiter's satellites, that formed one of the data upon which the velocity of light was determined, and which led to the discovery of its progressive motion. The earth's motion, in reference to that of light, gives rise to the phenomena of *aberration*, for the earth will have moved a certain distance in her orbit during the time that a ray of light, which renders a star visible, is passing from it to the observer; consequently the *apparent* differs from the *real* place of a star.

Some bodies intercept light, or are *opaque*; others allow its transmission, or are *transparent*; and there are gradations from perfect opacity to nearly perfect transparency, as we see in *semitransparent* or *translucent* bodies.

But although we are in the habit of using the terms *perfect transparency* and *perfect opacity*, such states do not in fact exist; for the air, glass, water, and similar media, all arrest or absorb certain portions of light; whence it is inferred that perfect darkness may prevail in the depths of the ocean; and on the other hand, that the most opaque substances, if sufficiently attenuated or extended, would transmit light, as is the case with gold, and with exceeding thin laminæ of some other metals.

The transmission of light in right lines is evident from the phenomena of the shadows of opaque bodies, and its intensity diminishes as the squares of the distance. Thus, if an opaque screen one foot square be placed at a certain distance from a light, *a*, it will exactly shadow a second screen, two feet square at double the distance; a screen three feet square at thrice the distance, and one of four feet square at four times the distance; that is, the light concentrated upon the first screen would extend itself over four times the space, if suffered to fall upon the second, over nine times upon the third, and over sixteen times upon the fourth.

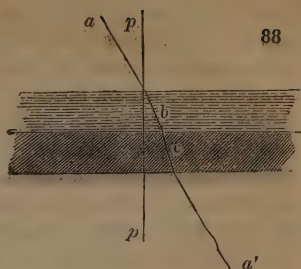


REFRACTION OF LIGHT.—When a ray of light passes through the same medium, or when it passes perpendicularly from one transparent medium into another, it continues to move without changing its direction; but when it passes *obliquely* from one medium into another of a different density, it is thrown more or less out of its old direction, and is said to be *refracted*. The refraction is *towards* the perpendicular when the ray passes into a denser medium, and *from* the perpendicular when it passes into a rarer medium. The medium in which the rays of light are caused to approach nearest to the line perpendicular to its surface, is said to have the greatest refractive density.

In the following diagram, fig. 88, *a* represents the oblique ray passing through *air*, and entering *water* at *b*, and *glass* at *c*, and emerging into the *air* at *a'*. *p.p* is a perpendicular line, towards which the ray is refracted, in the medium *b*, and to a still greater extent in the denser medium *c*; but

on again emerging into air at a' , it turns from the perpendicular, and resumes its former line of passage.

We accordingly find that when the ray a traverses one and the same medium, differing in different parts in its *density*, it will suffer a deflection in various parts of its course proportionate to the density of the medium. We know that the density of the atmosphere is greatest at the earth's surface, and that it decreases as we ascend, gradually becoming more and more attenuated; hence, supposing the temperature uniform, the refractive power of the atmosphere would be greatest at the earth's surface, and gradually diminish as we recede from it; a ray of light, therefore, passing obliquely from a celestial object and falling upon this variable atmosphere, would be gradually more and more bent in its passage through it, and move in a curved line, exactly as if the atmosphere consisted of an infinite number of layers, gradually increasing in density from above downwards.



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It is this deflection, or refraction of light, that causes bodies to appear bent or distorted when viewed through transparent media, such as water or glass: an object, for instance, seen through a prism, seems more or less thrown out of its real place; and a stick, plunged into water, looks as if it were bent or broken. For the same reason, a piece of money, placed at the bottom of a basin, appears to be raised when water is poured upon it; so that if, in the first instance, the eye be so placed, in reference to the edge of the basin, as just to see the further edge of the coin, on pouring water into it, the whole of it will be visible: by spirit of wine it will appear to be still more raised than by water; and by oil, more than by spirit.

In viewing objects, therefore, through refracting media, they are always more or less thrown out of their real places; and, in consequence of atmospheric refraction, the sun and stars are visible before they actually emerge from, and after they have sunk beneath, the horizon; and as, on the one hand, in consequence of the progressive motion of light, and the great distance of the objects, celestial phenomena are not seen till an appreciable time after their actual occurrence; so, on the other, in consequence of refraction by the atmosphere, they are not seen in their real places; with the exception, indeed, of stars in the zenith. These displacements are so trifling as to be disregarded in ordinary cases, but they require strictly to be taken into the account in astronomical calculations.

The ultimate direction of a refracted ray of light is influenced by the relative position of the surface of the refractor, both at its point of entrance and exit. Thus by refraction at convex surfaces the rays may be converged to a focus, as by a common lens, the refraction in these cases taking place, as if each ray fell upon a plane surface tangent to the curve at the point of incidence.

The density of bodies is by no means the only circumstance that affects their refractive power, it also depends upon their chemical nature; and,

generally speaking, those substances have the greatest refractive power which are combustible, or which contain an inflammable basis. Nor is the refractive power of *compounds* the mean deduced from that of their components; which, however, it generally is, in mere *mixtures*. Hydrogen, sulphur, phosphorus, diamond, bees'-wax, amber, oil of turpentine, camphor, linseed oil, and olive oil, have refractive powers from two to seven times greater in respect to their density than those of most other substances. Newton, observing the high refractive power of the diamond, inferred that it was "an unctuous substance coagulated," long before its combustibility and real nature were known. This law seemed at one time to be opposed by an observation of Dr. Wollaston respecting *phosphorus*, which led him to ascribe to it a low refractive power; but Sir D. Brewster, confiding in the truth of the generalization, found, by forming it into prisms and lenses, that its refractive power was double that of the diamond when compared with its density. The following is a table of the refractive powers of many of the gases and vapours, that of atmospheric air being 1000, from the experiments of Dulong.—(*Bulletin Philom.* 1825; *Ann. de Ch. et Phys.*, xxxi., 154; *Gmelin Handbuch*, i. 139.) If the refractive power is directly as the density and inflammability (implying by that term, attraction for oxygen or electro-positive power,) it is, perhaps, = the product of the density into the inflammability; in which case the latter will be found by dividing the refractive power by the density; and, in column E, hydrogen presents itself as the most electro-positive, and oxygen as the most electro-negative, body, and the other quotients agree with this, excepting nitrous oxide, which appears more electro-positive than nitrogen. It appears from column C, that the actual refractive power of a compound exceeds the calculated, when the compound is neutral or alkaline, but falls short of it when it is acid, which also indicates an electro-chemical relation to it.

A	B	C	D	E
Air	1.000		1.000	
Oxygen	0.924		1.103	0.83
Hydrogen	0.470		0.068	6.89
Steam	1.000	0.933	0.625	1.60
Carbonic oxide	1.157		0.972	1.19
Carbonic acid	1.526	1.619	1.524	1.00
Olefiant Gas	2.302		0.980	2.35
Carburetted hydrogen	1.504		0.559	2.69
Sulphuretted hydrogen	2.187		1.178	1.85
Sulphurous acid	2.260		2.247	1.01
Sulphuret of carbon vapour	5.179		2.644	1.96
Chlorine	2.623		2.470	1.07
Muriatic acid gas	1.527	1.547	1.254	1.22
Phosgene gas	3.936	3.784	3.442	1.14
Nitrogen	1.020		0.976	1.04
Nitrous oxide	1.710	1.482	1.527	1.12
Nitric oxide	1.030	0.972	1.039	0.99
Ammonia	1.309	1.216	0.591	2.22
Cyanogen	2.832		1.818	1.55
Hydrocyanic vapour	1.531	1.651	0.944	1.62
Alcohol vapour	2.220		1.613	1.37
Ether vapour	5.280		2.580	2.05
Muriatic ether vapour	3.720	3.829	2.234	1.67

[In the preceding column A specifies the gas, B its refractive power determined by experiment, air being = 1. C shows the calculated refractive power, deduced from that of the component gases. D the density compared with air. E the quotient of the refractive power divided by the density.]

The following are the refractive powers of several gaseous bodies, from the experiments of Biot and Arago, at the temperature of 32° F., and under mean barometrical pressure, corresponding to column E of the preceding table.

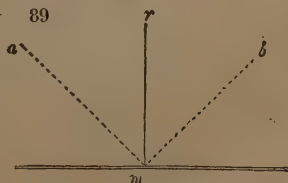
Atmospheric air	1.00000	Ammonia	2.16851
Oxygen	0.86161	Carbonic acid	1.00476
Nitrogen	1.03408	Carburetted hydrogen	2.09270
Hydrogen	6.61436	Muriatic acid gas	1.19625

Dr. Wollaston invented an apparatus in which, by means of a rectangular prism of flint-glass, the index of refraction of substances may be read off at once by a vernier, the three sides of a moveable triangle performing the operation of reduction in a very compendious manner. As the chemical constitution of bodies may in many instances be inferred from their refractive power, Dr. Wollaston has suggested the application of such an instrument for discovering the purity of essential oils: in oil of cloves, for instance, he found a wide difference in refractive power, that of the genuine oil being as high as 1.535, while other samples did not exceed 1.498, and were probably adulterated. (*Phil Trans.* 1802.) In thus employing this instrument, however, it must be recollected that the refractive power of the same oil distilled at different times will vary, this, at least, I have found to be the case with oil of peppermint.

The following table shows the refractive powers of several liquids and solids.—(DANIELL, § 225.)

Sulphuret of Carbon	1.678	Chromate of lead	2.974
Tolu balsam	1.628	Diamond	2.439
Castor oil	1.490	Phosphorus	2.224
Almond oil	1.483	Calcareous spar	1.654
Oil of turpentine	1.475	Quartz	1.548
Sulphuric acid	1.434	Rosin	1.559
Alcohol	1.372	Rock salt	1.557
Ether	1.358	Ice	1.308
Water	1.335	Tabasheer	1.111

REFLECTION OF LIGHT.—When the rays of light arrive at the surfaces of bodies, a part of them, and sometimes nearly the whole, is thrown back, or *reflected*, and the more obliquely the light falls upon the surface, the greater in general is the reflected portion. In these cases the angle of reflection is always equal to the angle of incidence. Suppose a ray of light to impinge *perpendicularly* upon the surface of a mirror, as at *r m*, but one ray is seen, for the ray of incidence and that of reflection are both in the same line, though in opposite directions, and they are confounded together. The ray therefore which appears single, is, in fact, double, being composed of the incident ray proceeding to the mirror and the reflected ray returning from it. These rays may, however, be separated by so holding the mirror that the incident ray,



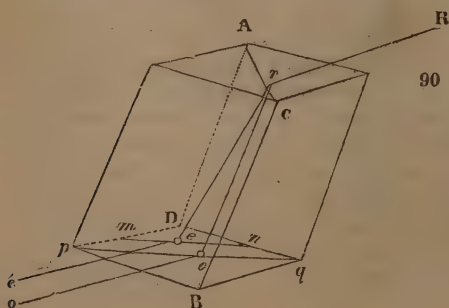
a m , shall fall *obliquely* upon it. in which case the reflected ray, $m b$, is thrown off in the opposite direction. If a line be drawn from the point of incidence, perpendicular to the mirror (as the line $m r$), it divides the angle of incidence from the angle of reflection, and both are seen to be equal.

When rays of light fall upon a concave mirror, they are reflected as if from a series of planes tangents to that surface, and may thus be *converged* to a point or focus; when, on the other hand, the rays fall upon a convex mirror the convergency of the rays is diminished, and their divergency increased.

§ 13.—DOUBLE REFRACTION AND POLARIZATION OF LIGHT.

IN all cases of the *ordinary* refraction of light, the ray by which we see an object through a refracting medium, although bent, yet, in pursuing its course to the eye, does not quit a plane perpendicular to the refracting surface: the plane in which the eye, the object, and the point on the surface of the medium in which the object is seen are contained, is an upright, or vertical plane. (See HERSCHEL'S *Discourse*, p. 30.) But there are certain *crystalline* substances, as rock-crystal, &c., but especially *Iceland spar*, which possess the remarkable property of *doubling* the image, seen through them in certain directions; so that, instead of seeing one, we see two, side by side, when such a crystal is opposed between the object and the eye: and if a ray, or small sunbeam, be thrown upon a surface of this substance, it will, on traversing it, be split into two, making an angle with each other, and each pursuing its own separate course.

Having obtained a rhomb of Iceland spar, fit for these experiments, place it, as shown in fig. 90*, above a sharp line, and look through it with the eye about R. The line will appear doubled, like $mnpq$. So also a dot will be doubled, as eo . If we cause a ray or pencil of light, R, r , to fall upon the surface of the rhomb. it will be separated into two rays or pencils, ro, re each of which will emerge from the rhomb at o and e ,



in the directions oo' and ee' parallel to rr . The ray Rr , therefore, has suffered *double refraction* in passing through the rhomb: and as the very same phenomena will take place by making the ray Rr fall at the same incidence and in the same direction, relative to the summit A, upon any point of the faces, it is manifest that the double

refraction cannot arise from any difference of density in different parts of the rhomb.

* See *Library of Useful Knowledge*, on the double refraction and polarisation of light.

Of the doubly-refracted rays, *one* always appears to follow the same rule as if the substance were glass or water, and retains the plane perpendicular to the refracting surface: the other ray, on the contrary, which is therefore said to have undergone *extraordinary refraction*, does quit that plane, and its deviation becomes subject to a new law. It has, however, been demonstrated by Fresnel, that in the greater number of instances of double refraction by crystalline bodies, neither of the images follows the ordinary law, but both undergo a deviation from their original plane, and acquire new properties, and this is the case with respect to Iceland crystal, as we shall presently find; we may, however, continue the terms *ordinary* and *extraordinary ray*, for convenience sake.

Some remarkable effects accompanying double refraction, led Newton to conceive the singular idea, that a ray of light, after emerging from the crystal, acquires *sides*; that is, distinct relations to surrounding space, which it carries with it through its whole subsequent course, and which give rise to all those complicated and curious phenomena now known under the term *polarization of light*. This idea, however, appeared so extraordinary, and as Sir J. Herschel remarks, offered so little handle for further inquiry, that the subject dropped, till Malus, in 1810, announced the discovery of the *polarization of light by ordinary reflection*, at the surface of a transparent body. He found that when a beam of light is *reflected* from the surface of such a body, *at a certain angle*, it acquires the same singular property which is impressed upon it in the act of double refraction, and the phenomena of polarization are in this way more conveniently exhibited*.

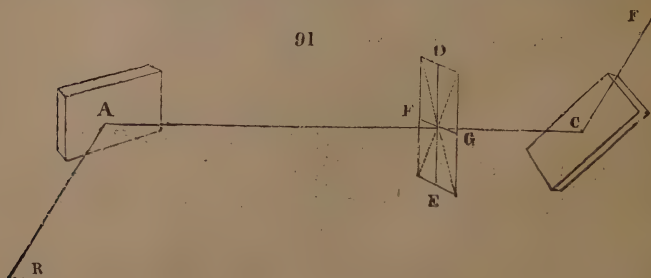
In general, when a ray of light is reflected from a pane of plate-glass or other polished surface, it may be reflected a second time from another surface; it will also pass freely through transparent bodies: but if a ray of light be reflected from a pane of plate-glass, at an angle of 57° , it is rendered incapable of reflection at the surface of another pane of glass, in certain definite positions, but is reflected by it in other positions: it also loses the power of passing through some transparent bodies in certain positions whilst in others it is freely transmitted by them.

If a prismatic crystal of transparent brown *tourmaline*, be cut longitudinally (that is parallel to the axis of the prism) into plates about the thirtieth of an inch thick, and the surfaces polished, luminous objects may be viewed through them. If one of these plates be held perpendicularly between the eye and a candle, and turned slowly round in its own plane, no change will take place in the image of the candle; but, if the plate be held in a fixed position, with its axis or longitudinal section vertical, when a second plate is interposed between it and the eye, parallel to the first, and turned slowly round in its own plane, a remarkable change is observed in the nature of the light, for the image of the candle vanishes and reappears alternately at every quarter of a revolution of the plate, varying through all degrees of brightness, down to total, or almost total evanescence, and then increasing again as it had before decreased. These appearances depend upon the relative position of the plates: when their longitudinal sections are parallel, the brightness of the image is at its

* The following details connected with this subject, I have abridged from Mrs. SOMERVILLE's *Connexion of the Physical Sciences*, Section xxii.

maximum, and when they cross at right angles it vanishes. Thus, the light, in passing through the first plate of tourmaline, has acquired a property totally different from the direct light of the candle: the direct ray would have penetrated the second plate in all directions, whereas the refracted or *polarized* ray penetrates it in certain positions only, and in others is wholly obstructed. The plate of tourmaline therefore becomes, when applied as above directed, a test of the polarization of the ray. If we now look at the two images produced by the Iceland spar, through a plate of tourmaline, it will be found, that as the tourmaline revolves, the images vary in their relative brightness; one increases in intensity till it arrives at a maximum, whilst the other diminishes till it vanishes, and so on alternately at each quarter of a revolution, showing that *both of the images are polarized* in opposite directions, for in one position the tourmaline transmits the ordinary ray, and reflects the extraordinary; and after revolving 90° , the extraordinary ray is transmitted, and the ordinary ray is reflected.

If a pane of plate-glass, with its lower side blackened, or lying upon a piece of black cloth, be placed on a table, and a candle near it, the rays of which fall upon the glass at an angle of 57° , it will be found that they are reflected from the surface in a polarized state, for, on viewing the image through the revolving slice of tourmaline, it will disappear at every quarter of a revolution. It is also found that this polarised ray is incapable of being reflected a second time from another plate of glass, placed at the same angle. If, for instance, the second plate be so placed as to make an angle of about 57° with the reflected ray, the image of the first pane will be reflected in its surface, and alternately illuminated or obscured at every quarter of a revolution of the second plate, according as its plane of reflection is parallel or perpendicular to the plane of polarization. Hence, polarized light is shown to be incapable of reflection in a plane at right angles to the plane of polarization. These, and some other curious phenomena of polarized light are easily shown by the following arrangement of apparatus. Let two plates of glass, blacked on the back, AC, be arranged as in the following diagram, fig. 91, so that the rays from a candle at R, falling upon the first or *polarizing* plate, A, at its angle of polarization, may not be reflected by the second or *analysing* plate, C. This adjustment may be made by looking into C in the direction of FC,



and finding the image of the candle wanting; then take a thin film of mica, or sulphate of lime, DEFG, and place it between the two plates,

perpendicular to the polarized ray. It will then be found, on turning this plate upon its axis, that the image of the candle disappears, and reappears at each quarter of a revolution; or, in other words, that in certain positions it *depolarizes* the ray. Common glass is generally incapable of effecting this depolarization, but it acquires the depolarizing power when submitted to pressure, or heated, or when it has been heated and very suddenly cooled; the influence of its particles upon those of light becoming then analogous to crystallized bodies. If we now view the polarized image through a plate of tourmaline, with the interposed plate of mica, a succession of beautiful colours will appear in certain positions of the mica, depending upon the thickness of the plate: these colours succeed each other in definite order, and are complementary to each other.

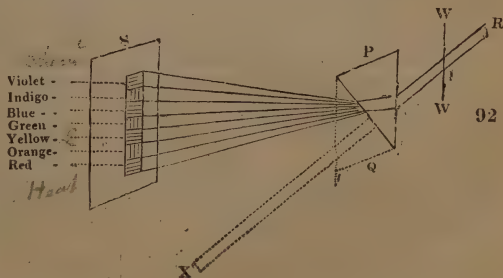
Different reflecting surfaces polarize light at different angles: thus the angle for water is $53^{\circ} 11'$; for glass $56^{\circ} 45'$; for rock crystal $56^{\circ} 58'$; for Iceland spar $58^{\circ} 51'$; for diamond $68^{\circ} 1'$; for sulphur $63^{\circ} 45'$.

In the preceding details, my object has been merely to explain the meaning of the term *polarization*, as applied to certain properties of light; those who would pursue the inquiry will find it amply treated of in the communications of Sir David Brewster to the Royal Society (*Phil. Trans.* 1813, &c.), and in various treatises to which references are given in the authorities which I have had occasion to quote. I must also refer to the same sources, for the discussions to which the investigations connected with the subject have given rise, respecting the nature of light; they are extremely curious and important, especially as illustrative of the applications of the undulatory theory.

§ 14.—DECOMPOSITION OF LIGHT.

THAT a sun-beam, in passing through certain dense media, gives rise to a series of brilliant tints, similar to those of the rainbow, was known in the earliest ages, but Newton first explained and investigated the phenomena. He admitted a ray of light, *r*, fig. 92, through a hole in the window-shutter, *w*, of a dark room, and caused it to fall upon a glass prism, *P*, by which it was refracted, and resolved into *seven* colours, which formed an oblong image or *spectrum* upon the white screen, *s*, in the order represented, namely, red, orange, yellow, green, blue, indigo, and violet. Had the ray proceeded straight onwards it would have formed a luminous spot at *x*, it is, therefore, seen that of these coloured rays, the *violet* have undergone the greatest refraction, and the *red* the least, and that they are arranged in the order of their refrangibility.

Newton submitted each of these rays to repeated refractions, but found that they were not resolvable into simpler colours; but, on causing them to pass through a second prism



in an inverted position *Q*, or by collecting them into one focus by means of a lens, they were reunited and again produced *white light*; whence he inferred white light to consist of these seven simple or primitive colours. With the prism which he used, (of flint glass,) the respective lengths of the colours (dividing the spectrum into 360 parts) were as follows:—red 45, orange 27, yellow 40, green 60, blue 60, indigo 48, violet 80. These spaces, however, cannot be very accurately defined, as the colours imperceptibly shade into each other: they also vary with prisms of different substances. The composition of white light by the union of the above colours, may be also shown by mixing seven different powders, having the colours and proportions mentioned; or more readily, by painting the rim of a wheel with the seven colours, which, when in very rapid motion, appears white, or nearly so*.

The *colours* of bodies were referred by Newton to their relative absorbent and reflective powers, in respect to these rays; he supposed *black* surfaces to absorb, and *white* to reflect them all, and that other colours are produced by the absorption of all the rays except those of the observed colour, which are presumed to be reflected. And in respect to transparent media, those which are colourless suffer the light to pass unchanged, while those which are coloured, transmit some rays, and absorb others. The absorption of coloured rays, therefore, by certain media, furnishes another means of analysing light, and from experiments conducted in this way, Sir David Brewster has been led to conclude that the only colours of the spectrum which can properly be called *simple*, are the red, yellow, and blue; that they are concentrated in those parts of the spectrum where each appears, but that they are also spread more or less over the whole, and that the orange results from a mixture of red and yellow; the green, from a mixture of yellow and blue; and the violet and indigo from red and blue, with a trace of yellow.

The length of the spectrum depends upon the nature of the prism or refracting medium; thus, if obtained by a hollow prism of glass, filled with oil of cassia, it is much longer than when glass only is used; hence the oil of cassia is said to *disperse* the rays more than glass, or to have a greater *dispersive power*. In such cases, also, the coloured spaces bear a very different ratio to each other.

It appears from the experiments of Sir W. Herschel, (*Phil. Trans.*, 1800,) that the greatest *illuminating* power of the spectrum is in the brightest yellow, and that it decreases towards either extremity, the blue and red being nearly equal, and the violet inferior to both.

A curious fact respecting the prismatic spectrum, when very perfect, and the sunbeam small, was discovered by Professor Frauenhofer, of Munich; he observed it to be irregularly subdivided by a number of black lines; they are so narrow as to escape observation without great care; they are seen when the spectrum is received upon the object-glass of a telescope, or by viewing a narrow slit between two nearly-closed shutters,

* The impression of light upon the retina of the eye continues for about an eighth part of a second, so that a luminous point revolving with a velocity sufficient to complete the circle within that time, appears not as a point, but as a circle of light, the impression made on it in every point of its revolution being retained for the above time.

through a very perfect prism, held close to the eye, with its refracting angle parallel to the line of light. They are always found in the same parts of the spectrum, of the same breadths and intensities. They are very numerous, amounting to some hundreds; from these, Fraunhofer selected seven, and determined their distances so accurately, that they form invariable points of reference for measuring the refractive powers of different media. They are also seen in the light of the stars, in electric light, and in the flame of combustible substances, though in each case differently arranged, each having a system of them peculiar to itself, and remaining the same under all circumstances.

§ 15.—CHEMICAL EFFECTS OF THE SOLAR RAYS.

THE object of the preceding sections has been to give an outline of the principal physical properties of light, or at least of such of them as have bearings upon chemistry. We may now proceed to the consideration of some other phenomena connected with, or dependent upon, the solar rays.

No one can have failed to observe the differences between *vegetables* thriving in the full enjoyment of solar light, and those which grow in obscure situations, or which are entirely deprived of its agency. The former are of brilliant tints, the latter dingy and white; in the one, the various secretions come to perfection; in the other they are either modified or disappear. Of this, numerous familiar instances might be cited, especially among our esculent vegetables. The shoots of a potato produced in a dark cellar are white, straggling, and differently formed from those which the plant exhibits under its usual circumstances of growth. Celery is cultivated for the table by carefully excluding the influence of light upon its stem: this is effected by heaping the soil upon it so as entirely to screen it from the solar rays; but if suffered to grow in the ordinary way, it soon alters its aspect, throws out abundant shoots and leaves, and instead of remaining white and of little taste, acquires a deep green colour, and a peculiarly bitter and nauseous flavour. The interior, or heart of endive is not eatable, unless protected from light; if exposed to it, it becomes disagreeably bitter and tough. The heart of the common cabbage is another illustration. The rosy and coloured aspects of the side of fruits exposed to the sun are referable to the same cause. Changes yet more remarkable have been observed in plants vegetating entirely out of the access of light. In visiting a coal mine, Professor Robinson found a plant with a large white foliage, the form and appearance of which were quite new to him: it was left at the mouth of the pit, when the subterranean leaves died away, and common tansy sprung up from the root.

In the *animal creation* the influence of light is equally evident. It is curious to remark the dull and dingy tints of polar and subterranean animals, as contrasted with the gaudy and brighter colours of those which inhabit the tropical regions of the globe, and enjoy the full sunshine. In the human species, too, a due quantity of light is requisite to health; miners are generally pallid and unhealthy; and the inhabitants of the dark alleys and courts of London indicate a similar want of its beneficial

influence; though in these cases, bad air and poor diet also contribute to want of health.

In reference to the above and other effects of light upon plants, there can be little doubt that they chiefly depend upon its power of modifying the chemical changes, which are constantly carrying on in the vegetable kingdom; but the common operations of the laboratory furnish us also with some striking illustrations of *the influence of light in promoting the chemical agencies of bodies.*

Hydrogen and *chlorine* are two gases, which, when mixed and kept in the dark, are nearly without action; but if exposed to the light of day, they soon act upon each other, and unite to form *hydrochloric acid*; and if the sun shines directly upon the bottle containing them, it not unfrequently happens that they inflame and explode in consequence of the energy imparted to their attraction by the solar rays. We have an analogous instance in *chlorine* and *carbonic oxide gas*, which, when mixed together, remain without action till exposed to light; they then combine chemically with diminution of volume, and produce a compound, which, from the mode of forming it, has been termed *phosgene gas*. In the same way also, chlorine and water react rapidly upon each other in the sunshine, forming hydrochloric acid and evolving oxygen.

Some of the salts of gold and of silver, especially their chlorides, are remarkably susceptible tests of the chemical agency of light: the *nitrate of silver* may be selected by way of illustration. If a piece of paper be dipped into a solution of this salt, and kept in the dark, it suffers no apparent change; but if exposed to light, it soon becomes purple, brown, and black, changes of colour depending upon a chemical change suffered by the salt. A pretty experiment, showing the action of light upon nitrate of silver, was devised by Mr. Wedgwood: a piece of paper, or other convenient material, was stretched upon a frame and sponged over with a solution of the salt; it was then placed behind a painting upon glass; and the light, traversing the painting, produced a kind of copy of it upon the prepared paper; those parts in which the rays were least intercepted being of the darkest hues. Many improvements in these *photogenic drawings*, as they have been termed, have been effected more especially by Mr. Fox Talbot, Sir John Herschel, and Mr. Alfred Taylor, some of the details of which will be found under the head of *SILVER*; as also an account of the extraordinary phenomena discovered by M. Daguerre, in reference to the action of light upon a surface of silver covered by a film of iodine.

Scheele was the first to whom the ingenious idea occurred of ascertaining whether all the rays possessed similar chemical powers, or whether they belonged more exclusively to one colour than to another; and he found, upon refracting a beam by the prism into its primary colours, and throwing them upon a piece of paper prepared with nitrate of silver, that the greatest blackening effect was produced by the *violet ray*, and that the decomposing or chemical powers of the prismatic *spectrum*, gradually decreased towards the red ray, where scarcely any effect was produced. This result was quite contrary to expectation; for one would, of course, have anticipated the greatest effect in the most luminous part of the spectrum.

It was afterwards discovered by Wollaston and Ritter, (*Phil. Trans.*, 1802, and *Philos. Journal*, iv. and viii.,) that certain *invisible* rays, occupying a place in the spectrum just beyond the violet extremity, possessed a greater power of effecting the above and other chemical changes, than the violet rays themselves; and it has, consequently, been inferred that such distinct rays emanate from the sun, possessed, as their place in the spectrum shows, of great refrangibility: and that the coloured rays (and their mixture, constituting white light,) derive their chemical powers from the admixture of these highly refrangible and chemically acting rays, which are most abundant at the blue end of the spectrum, and gradually decrease towards the red or least refrangible rays. Thus, it was found that the greatest blackening effect upon the salt of silver was produced just beyond, and out of the violet ray: the other peculiar chemical effects to which we are now adverting were also most manifest in the same spot, It must, however, be observed, that the place occupied by these rays in the spectrum, depends, in some measure, upon the nature of the medium by which the light is refracted.

Berard found, that in the focus obtained by concentrating the rays of one-half of the spectrum (the red end), chloride of silver was not blackened, though the light was very brilliant; but that, in the darker focus from the violet half, it was immediately discoloured. Seebeck, by exposing chloride of silver to the red ray, found that it gradually acquired a pale rose colour; and that the rays coloured by transmission through coloured glasses, produced the same general effects as the differently coloured rays of the spectrum. He also found that a piece of paper, dipped in a neutral, and not too-concentrated solution of gold (which is reduced by light), underwent no change when preserved in the dark, provided it had not been previously exposed to light; but that, if exposed for a short time to the sun's rays, though not at the moment discoloured, and then kept in a dark place, it gradually became purple, and the gold was reduced. Ritter and Davy have assumed that the opposite ends of the spectrum possess opposed chemical powers, something like the opposed electrical poles, but of this we have, as yet at least, no satisfactory experimental evidence; it is true that Wollaston found a piece of paper stained yellow with tincture of guaiacum, to become green in the violet ray, and again yellow in the red; but he afterwards found that the mere heat of the red ray produced the effect; and many vegetable colours are as effectually bleached by heat as by light.

Many years ago, Morichini thought that he had communicated *magnetism* to steel-wires, by exposing them to the rays of violet light. So curious a result attracted much notice, and his experiments were repeated by several eminent philosophers with very various success: it was generally, however, presumed that he was mistaken in his conclusions, and that the needles had acquired magnetism from some other sources. The subject was afterwards resumed by Mrs. Somerville, (*Phil. Trans.*, 1826,) who, from a series of apparently well-conducted experiments, arrived at the same conclusion as Morichini. It must however, be confessed, that there are many difficulties in the way of attaining perfectly unexceptionable results in these experiments; and whether magnetism is, or is not, producible by the sole influence of light, is a question not definitively

settled, unless, indeed, the experiments of Messrs. Riess and Moser (*Edin. Journal of Science*, II., 225,) be considered conclusive in disproving it.

§ 16.—OF RADIANT MATTER AS A SOURCE OF HEAT.

Different parts of the prismatic spectrum have different heating powers.—If we cause the spectrum to fall upon a sheet of paper, and gradually pass the hand through it, from the violet to the red end, we shall perceive the latter to be sensibly warmer than the former; and, on applying a delicate thermometer in the differently coloured rays, it will be found scarcely affected by the blue; in the green it rises; and in the red, shows an increase of several degrees of temperature. Assuming the heating power of the violet rays, = 16° , that of the green is = 26° , and of the red = 55° .*

The observation of this fact suggested to Sir W. Herschel the possibility of the heating power of the spectrum extending *beyond* the red ray, and, on applying a thermometer just out of the red ray, and beyond the limits of the visible spectrum, this was found to be the case. A thermometer in the red ray rose *seven* degrees in ten minutes, but just *beyond* the red ray, the rise in the same time was *nine* degrees. *Phil. Trans.*, 1800†.

In these, as in the former experiments, the effects are modified by the nature of the prism used to refract the light: when it is of flint glass the phenomena are as above described; but, with crown glass, water, and other refracting media, the position of the heating or calorific rays varies.

It appears, then, that the radiant matter of the sun is resolvable, by refraction, into three distinct sets of rays; those producing *colour*; those which effect certain *chemical changes*; and those which excite *heat*; the chemically acting rays are the *most* refrangible, the calorific rays the *least* so, and the colorific rays, or those producing light and colour, possess a *mean* degree of refrangibility. All these rays are susceptible of refraction and reflection, as is proved by their concentration into a focus by a concave mirror or a lens; in which case, in consequence of their different refrangibilities, the heating and chemically acting focus is probably not identical with the luminous focus. From the experiments of Berard, Melloni, and Professor Forbes, the chemically acting and the heating rays are also susceptible of the phenomena of polarisation.

§ 17.—TERRESTRIAL RADIATION, AND THE INFLUENCE OF VARIOUS SURFACES UPON THE RECEPTION AND EMISSION OF RADIANT MATTER.

WE use the term *terrestrial radiation*, to designate the heat and light thrown off by terrestrial bodies under certain circumstances, especially at high temperatures, as when they are red-hot, or burning; that is, in a state of *ignition*, *incandescence*, or *combustion*. We also well know that

* Hence the idea of the different-coloured rays, consisting of light in combination with different proportions of heat.

† See also the repetition of these experiments by Sir H. Englefield, and by M. Berard. (*Thomson's Annals*, II., 163.)

terrestrial heat radiates from bodies at temperatures far below those required for ignition. If, for instance, I fill a jug with hot water, I feel heat emanating from it to my hand when held near it. All these subjects may be discussed under the head of *terrestrial radiant matter*.

The rays which emanate from heated bodies, whether attended or unattended by light, may be *reflected* in the same way as the solar rays, and the phenomena connected with this kind of radiation are, in many respects, extremely curious and important: they are also susceptible of many economical applications, for in this country it is to radiant heat that we are chiefly indebted for the warmth and comforts of our apartments in winter; the construction of our grates, and fire-places in general, being such as to carry away the whole current of the heated air by the chimney, and prodigally waste it in the atmosphere; they consequently produce their warming effects, by the heat which emanates from the burning fuel and heated surfaces, and is projected or radiated upon the surrounding bodies in the room.

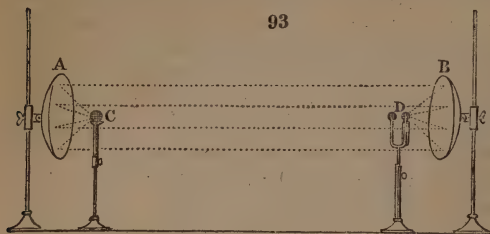
Several important facts upon the subject of the radiation of heat were established many years ago by Scheele (in his treatise on *air and fire*, originally published in 1777). He observed, that radiant heat passes through air without communicating heat to that medium, and that it is not intercepted by currents in the atmosphere. He then proceeded to ascertain how far it coincided with *solar* heat, in passing through glass, and found that, although the *light* of a fire or of a candle passed through it, their *heat* was arrested, or stopped in its progress. It was thus thought that a decided difference was established between solar and terrestrial heat; but we shall find that, in reference to this experiment, it is rather apparent than real, and due to the small quantity, or intensity of the latter, as compared with the former. He also found that, when a *glass* mirror is held before the fire, the light only is reflected, while the heat is absorbed, and the mirror itself becomes hot; but when for glass we substitute a mirror of *polished metal*, then, both the heat and the light are reflected, and the metal itself not heated: if, however, the surface of the metal be covered with some other substance, if it be smoked, for instance, by holding it over a burning candle, then the surface *absorbs* the rays of heat, and the mirror of metal, like that of glass, becomes itself hot.

These observations of Scheele led Leslie and others into the same path of inquiry, and we have, upon the whole, a very satisfactory series of experiments upon the subject, of which the following is an outline, as far as the principal facts are concerned:—

That heat radiates from bodies in right lines, and is susceptible of reflection, is shown by placing two polished concave mirrors, made of planished tin, or, what is better, of plated copper, exactly opposite to each other, and about ten feet asunder. For experiments upon a large scale, the mirrors should be at least of two feet diameter, but common tin mirrors or reflectors of one foot are sufficient for all common illustrations. A heated body, such, for instance, as an iron-ball, or a flask of boiling water, is placed in the focus of one mirror, and an air-thermometer in that of the other*. The rays of heat then impinge on the one mirror,

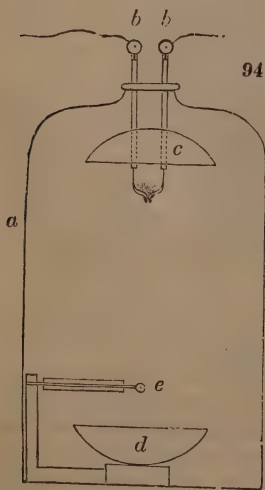
* The foci of the mirrors are best found by the help of a lighted candle, the heating focus corresponding with the luminous one; and in these experiments

and are *reflected*, consistently with the property of concave mirrors, in parallel lines, so as to fall upon the opposed mirror, whence they converge to its focus, in which is the thermometer, and which is affected proportionately to the heat of the original radiating body.



Let A, fig. 93, represent the first mirror; B the second; c the heated sphere or flask, and d the air-thermometer; the dotted lines show the direction of the calorific rays.

To prove that the thermometer is not affected by the *mere proximity* of the heated body, independently of any actual *reflection* let a sheet of pasteboard be held between the mirror B and the thermometer; the latter will immediately indicate the absence of the quantity of heat it before received, notwithstanding the source is as near to the bulb as it was before. If we even carry the ball a little out of the focus of the mirror A, by advancing it gently towards the thermometer, a diminution of heat will be perceived in the latter, in consequence of the disturbance of the most favourable arrangement for reflection. Indeed, the distance between the heated ball and the air-thermometer is such, that notwithstanding the delicacy of the latter instrument, it would not be affected, as may again be shown by removing one or both of the mirrors, and leaving the ball and thermometer in their same relative positions.



Radiation goes on from surfaces in all elastic media, and in vacuo, and is no way connected with aerial pulsations. By igniting points of charcoal by the voltaic battery in the focus of a small mirror confined in the exhausted receiver of the air-pump, Sir H. Davy found, that the receiver being exhausted to $\frac{1}{12}$ of the atmosphere, the effect upon the thermometer in the opposite focus was nearly three times as great as when the air was in its natural state of condensation. a, fig. 94, is the receiver, bb the insulated wires connected with the voltaic apparatus igniting the charcoal in the focus of the upper mirror c. In the focus of the lower mirror d is the thermometer e. A part at least of this increased effect is probably due to the increase of heat sustained by the charcoal, when thus ignited in vacuo, as compared with that which it acquires in the air.

the *differential thermometer* above described is most satisfactorily employed, for it is not affected by currents or ge-

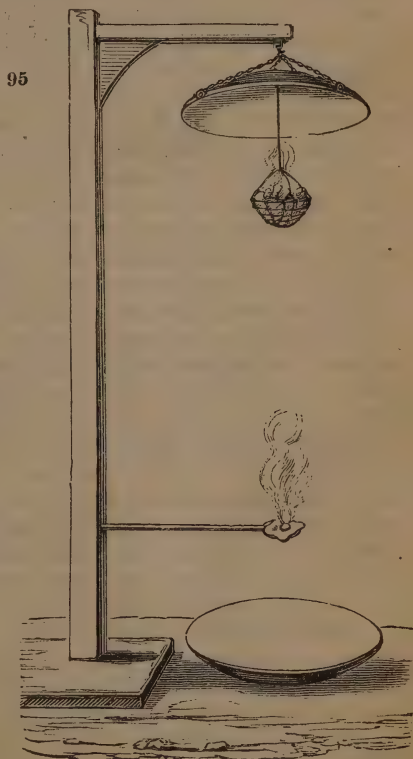
neral changes in the temperature of the room in which the experiments are made.

If, for the hot bullet, or flame of a candle, or flask of boiling water, we substitute some more copious source of heat, the effects will be proportionately great. If we, for instance, place a wire-basket full of burning charcoal, or a piece of red hot iron in one focus, and a piece of phosphorus in the other, the latter will be immediately inflamed; in the same way fulminating silver may be exploded, a mixture of chlorate of potassa and sulphuret of antimony inflamed, and even gunpowder kindled. And for such experiments we may adopt Sir H. Davy's plan of placing the mirrors vertically, as shown in fig. 95; the little chafing-dish is in the focus of the upper mirror, so that all the heat that reaches the lower mirror, and is concentrated in its focus, must be radiant and reflected, for the current of heated air will pass upwards and be lost.

For the conjugate mirrors we may occasionally substitute a sheet of burnished gold or silver paper, twisted up into the form of a truncated cone, with the metallic surface inwards: on holding its larger end towards a clear fire, or before a heated ball of iron, the radiant heat will be reflected so as to form a focus beyond the smaller end, where a piece of phosphorus or a lucifer match may be kindled.

The intensity of the calorific, as well as that of the luminous rays, decreases as the squares of the distance from the substance whence they emanate. A thermometer, for instance, placed at the distance of one foot from a heated body, will indicate the reception of four times more heat than at two feet, of nine more than at four feet, and of sixteen times more than at three feet. (See fig. 87.)

If we substitute a *cold body* for the heated one, a lump of ice, for instance, sprinkled over with salt, or a thin glass flask, containing a mixture of snow and salt, we shall then observe the thermometer in the opposite focus to be affected by *cold*; and this experiment has sometimes been adduced to prove that cold is a distinct form of matter. It has been supposed that highly attenuated emanations are at all times passing off from the surfaces of all bodies, under the form, and producing the effects of, *radiant matter*, the temperature excited by which depends upon that of the emanating body: that hot bodies radiate heat: that we perceive no effect from bodies at common temperatures, because their radiant matter is of the same temperature as that of the thermometer



or substance upon which they fall: but that cold bodies, on the contrary, throw off cold radiant matter, and hence their effect upon the thermometer. It has been assumed that the actual radiation of cold is proved by placing a plate of snow or bruised ice near the face, when an effect of cold is immediately perceived, and may be intercepted by a sheet of paper or other screen: that *temperature* therefore is merely a relative term: and that we may suppose ourselves in a temperature so high, that red-hot iron would radiate cold; or, again, in a temperature so low, that ice would radiate heat.

Sir. H. Davy observes, in reference to this subject, which he calls the *apparent* radiation of cold, "that if it be supposed that rays capable of producing heat emanate from all terrestrial bodies, but in quantities greater in some increasing proportion as their temperatures are highest, then the introduction of a cold body into the focus of one mirror, ought to diminish the temperature of a thermometer in the focus of the other, in the same manner as a black body placed in one focus would diminish the quantity of light in the other focus; and the eye is to the rays producing light, a measure similar to that which the thermometer is to rays producing heat." (*Elements*, p. 206.) Dr. Turner observes, that "the thermometer has its temperature lowered because it emits more rays than it receives, and it rises when the ice is removed, because it then receives a number of calorific rays, radiated by the warmer surrounding objects which were interrupted by the ice whilst it was in the focus." Mr. Daniell says, "the thermometer is the hotter body, and radiating its heat upon the nearest mirror, the rays are projected upon the second, and collected in the focus, where they are absorbed by the ice; and as no adequate return is made, the temperature of the thermometer necessarily falls."

INFLUENCE OF DIFFERENT SURFACES UPON THE RECEPTION AND EMISSION OF RADIANT HEAT.—It has been stated, that if a *polished metallic* mirror, of a concave or parabolic form, be held opposite the fire, it will give a heating focus, but that the mirror itself is long before it becomes sensibly warm; that is, the heat which impinges upon it, is immediately thrown off or *reflected*. If we now cover the surface of the mirror with an *unmetallic* coating, or merely roughen the surface, and then hold it towards the fire, a very different effect ensues, and now, the greater part of the radiant heat, instead of being thrown off, is *absorbed*, and soon heats the mirror. A mixture of chalk or lampblack and diluted glue or gumwater, answers very well for the above purpose.

Here, then, the *receptive* powers of surfaces, in regard to radiant matter, are shown materially to depend upon their nature or mechanical texture. In further illustration of this subject, a simple experiment may be made with the differential air-thermometer: let one of the glass bulbs, for instance, be nicely covered with a bright coating of gold-leaf, and leave the other in its usual state: place the instrument thus prepared upon a table, and bring a hot poker near it, taking care, however, that it is equally distant from both bulbs, or, if anything, rather nearer the metallic than the glass surface. Under these circumstances it will be found, that by far the greatest effect of heat is produced upon the *glass* ball, from which the fluid in the tube immediately recedes, notwithstanding

standing heat is equally applied to the gilt ball; the latter, however, refuses to absorb it, while the former imbibes it, and has its temperature proportionately augmented. If, instead of leaving the ball clean, it be covered with a thin coat of whitewash, or of lampblack, its receptive power will be still greater.

Although the *texture* of the surface is shown to be materially concerned in these results, it does not appear that *colour* in the least interferes; black-wash and white-wash are equally receptive of *terrestrial* radiant heat; nor does it appear to be absorbed in larger proportion by any one colour than by another.—(BACHE, *Journ. Franklin Institute*; May and November, 1835.) Dr. Stark indeed (*Phil. Trans.*, 1683) has endeavoured to show that *colour* does interfere in these cases; and he gives some curious statements respecting its influence upon the reception of *odours*; but it is possible that the texture and composition of the materials employed may affect the results; just as *white* silk is a much better insulator of electricity than *black* silk; not on account of colour, but of dye-stuff.

With regard to *solar* radiant heat, however, the case is different; and, as common experience teaches, *black* surfaces absorb it much more greedily than white, and the *temperature produced appears to be proportionate to the intensity of colour**. If pieces of cloth of different colours be exposed to the sunshine upon the surface of snow, the dark colours will sink into it, in consequence of the heat which they produce; the lighter colours scarcely effect the thawing of any portion; and white remains inactive. The difference between a white and black hat in heating the head, and between dark and light-coloured clothing in general, is well known to those who are much exposed to the summer's sun. Paint the bulb of one thermometer black, and of another white, and expose them to the sunshine; the former will indicate a higher temperature than the latter. A similar but more striking experiment may be made with the differential thermometer. Blacken one of the bulbs, and leave the other clean and transparent; if the instrument thus prepared be exposed to the sunshine, the excess of heat in the blackened ball is immediately indicated by the recession of the liquid from it to the clean ball. If the air thermometer be small and delicate, it is even susceptible of the mere impression of daylight, which, slightly augmenting the temperature of the black ball, depresses the fluid in the tube annexed to it. Hence the differential thermometer, thus constructed and applied, has been called a *photometer*†. Another illustration of

* It has hence been assumed, that the negro must suffer more from heat than the European; but it has been shown by Sir E. Home (*Lectures on Comp. Anatomy*), that the sun's rays are absorbed without ill effect, by the black rete mucosum, whereas they blister and scorch the white.

† Pictet first employed a blackened thermometer as a *photometer*. Leslie concluded, from his photometrical experiments, that the light of the sun pos-

sessed 12000 times the intensity of that of a wax-candle, so that a fragment of the sun, of the size of such a flame, would possess the illuminating power of 12000 candles. With the same instrument he determined the relative transparency of substances: thus he found, that of 100 rays of light, 80 passed through dry cambric, 93 through wet cambric, 49 through thin paper. 80 through oiled paper, &c.

this effect of solar rays, consists in placing a glass tube containing alcohol or ether in their focus, when collected by a lens; they traverse the transparent medium without heating it; but upon putting a piece of black paper into the liquid, or a strip of black wood or metal, it immediately boils. In this way water may be heated by directing the focus of a lens or mirror, exposed to the sun, upon good receptive and opaque surfaces immersed in it.

In many of the above statements there seems to be a manifest *difference* between solar and terrestrial radiant heat; but this is probably rather apparent than real; in the solar beam, radiant heat and light are combined, and when they fall upon dark surfaces are absorbed together. The quantity of radiant matter, too, emanating from the sun, is incomparably great in reference to anything produced artificially. The solar beam passes through a thin plate of glass without decomposition, and falling upon black surfaces upon the other side, is absorbed by, and heats them: but terrestrial radiant matter, emanating, for instance, from a lamp, or candle, or fire, suffers, in such case, a kind of decomposition; the *light passes* through the glass, but part of the *heat is stopped* in the progress; in the case of the sun's ray the transmitting glass is scarcely heated; in the other case, the glass becomes hot.

It was formerly supposed that terrestrial heat did *not* pass through glass, and that glass screens were as effectual as opaque ones in arresting the heat of the fire; but this is not so; the most intense artificial heat and light is probably that produced by charcoal ignited by voltaic electricity, and when a small lens is placed before a brilliant star of fire so obtained, and its focus thrown upon an air-thermometer, an elevation of temperature is always indicated. (Brande, *Phil. Trans.*, 1820.) Mr. Daniell has shown a similar effect in the rays from incandescent lime. (*Phil. Mag. N. S.*, ii. 59.)

There are other well known instances, in which the passage of common radiant heat through glass is evident; if we stand, for instance, upon the outside of a shop-window when a gas-burner within is suddenly lighted, we perceive the instantaneous impulse of heat upon the face; and there is no difficulty in causing radiant heat, even of low intensity, to permeate glass and other transparent media in very thin layers. It was supposed that in these cases the direct transmission of the radiant heat was apparent only, and that it, in fact, was absorbed by, and heated the glass, which therefore itself became the radiating surface; an objection ingeniously answered by Prevost, who transmitted the heat of a flame through a thin sheet of water, issuing from a jet, so that the nature of the medium, as well as its constant motion, prevented all possibility of the transfer of the heat by any other method than direct radiation.

Newton conceived that radiant matter consisted of *particles* emanating from luminous and heated bodies with prodigious velocity; these particles he imagined might be of different sizes; the smallest, constituting chemical rays and violet light, being the most refrangible; the larger ones forming red light and heat, and being the least refrangible; and some have assumed that the matter emanating from terrestrial bodies might be so constituted as to be arrested by those transparent media

which allow a ready passage to solar rays. Newton put the query, "Whether light and common matter are not convertible into each other?" And, if we consider sensible heat in bodies to depend upon vibrations of their particles, a certain intensity of vibrations may send off particles into free space; and particles moving rapidly in right lines, may in losing their own motion, communicate a vibratory motion to the particles of terrestrial bodies."—(DAVY'S *Elements*, p. 215.) The explanation of the phenomena of radiant heat upon the undulatory theory, will be evident from what has been above stated.

But our knowledge respecting the transmission of heat through different media has been lately much extended by the profound and important researches of Melloni. (TAYLOR'S *Scientific Memoirs*, i. and iii.) He has shown that heat which has passed through one plate of glass becomes less susceptible of absorption in passing through a second. Thus, of 1000 rays of heat from the flame of oil, 451 were intercepted in passing through four plates of glass of equal thickness, of which 381 were intercepted by the first plate, 43 by the second, 18 by the third, and 9 by the fourth. But the most remarkable of Melloni's discoveries is that of the transmission of radiant heat through certain transparent bodies almost without impediment, while others, physically analogous, resist its passage; nor is this passage of heat dependant upon their transparency in regard to light: the latter are *diaphanous*, the former *diathermanous*. Thus, plates of the following transparent substances, each being 0.1031 of an inch in thickness, allowed very different portions of the rays of heat from an argand lamp to traverse them. Of 100 incident rays,

Rock salt	transmitted	92	Emerald	transmitted	29
Mirror glass	"	62	Gypsum	"	20
Rock crystal	"	62	Fluor spar	"	15
Iceland spar	"	62	Citric acid	"	15
Brown rock crystal	"	57	Rochelle salt	"	12
Carbonate of lead	"	52	Alum	"	12
Sulphate of baryta	"	33	Sulphate of copper	"	0

A slice of brown rock crystal, nearly opaque in regard to light, and 58 times thicker than a transparent plate of alum, transmitted 19 rays, while the alum only transmitted 6.

Melloni found the proportion of heat from different sources, which passes through a plate of glass 1-50th of an inch in thickness, to be as follows:—

	Transmitted.	Absorbed.
Of 100 rays from the flame of an oil lamp	54	46
" Red-hot platinum	37	63
" Blackened copper heated to 732°	12	88
" Ditto ditto to 212°	0	100

Rock salt is the only substance whose powers of transmission are the same for heat from all sources and all intensities, 92 per cent. of the incident heat passing through that substance, whether radiating from a bright flame or from the hand: sulphate of copper, on the contrary,

notwithstanding its transparency as regards light, is *athermanous*, or opaque, as regards heat.

It appears probable that these remarkable differences are rather the result of mechanical structure than of chemical composition, for when a block of common salt is divided into flakes, it arrests calorific radiation. The extraordinary properties of rock salt in regard to radiant heat render it invaluable in these researches; it constitutes "the true glass of radiant heat," and may be cut into lenses and prisms, and used for concentrating heat of all intensities, and decomposing it by double refraction, exactly as glass is in regard to solar rays.

Of 100 rays of heat from the same source, successively incident on water, alcohol, ether, bisulphuret of carbon, and chloride of sulphur, the transmitted rays were 11, 15, 21, 63, and 63. The rays transmitted through similar plates of coloured glass, were with violet glass 53, with red 47, with yellow 34, with blue 33, and with green 26.

It would further appear from Melloni's experiments, that as there are varieties of light characterized by different colours, so there are different kinds of radiant heat dependent upon the sources whence it emanates. Rays of light which have passed through blue glass, will pass more readily through a second blue glass than through one of a different colour; and calorific rays which have passed through water, will pass more readily through a second stratum of water than through other liquids otherwise more diathermanous. Hence it follows that comparatively little additional heat is absorbed either by increasing the number or thickness of screens of the same material.

Having stated these facts concerning the receptive and transmitting powers of bodies in regard to radiant heat, we may now turn our attention to their emissive energies, and we shall find, that those bodies which have their temperatures most easily raised by the action of rays producing heat, are likewise those which are most easily cooled by their own radiation; or which, at the same temperature, emit most calorific rays; in other words, the *receptive* and *emissive* powers of surfaces, in regard to radiant heat, are co-existent and co-equal.

From what is stated above, it will appear that, if we place two similar metallic vessels filled with water before the fire, the surface of one of the vessels being clean and polished, and that of the other covered with a thin coat of lampblack, the former will receive heat much more slowly than the latter: a blackened saucepan set near a clear fire has its contents much sooner heated than a clean and bright one in the same situation.

Let us now reverse the experiment, and fill the blackened and the polished vessel respectively with hot water, and putting a thermometer into each, leave them upon a table at a distance from each other, and not near the fire. We shall soon observe that the thermometer falls most rapidly in the blackened vessel, and that it becomes cool much sooner than the other. Perhaps a simpler way of showing this fact, consists in painting one-half of the surface of a convenient tin or pewter vessel with a mixture of lampblack and gum-water, and leaving the other half or side clean and polished; if it then be filled with boiling water, no very delicate instrument is requisite to prove that heat is thrown off much more quickly from the unmetallic than from the metallic sur-

face; for the hand brought near the former feels a much greater impression of heat than when at an equal distance from the latter.

If we paste writing-paper, linen, or thin woollen cloth, or flannel, upon one half or side of a canister, and leave the other side clean, a very similar effect will be observed, for those surfaces radiate much more than metals; and, accordingly, a differential thermometer brought near a canister so prepared, will be affected at a much greater distance by the covered than by the clean surface.

The mutual relation of the receptive and emissive powers of bodies in regard to radiant heat, is well shown by a form of experiment devised by the late Professor Ritchie (*R. S. Journal*, v. 305). For the glass bulbs of a differential thermometer he substituted two hollow discs of thin metal plate: the surface of one of these discs was bright, and of the other coated with lampblack. Between these discs he placed a similar one filled with hot water, of which also one of the surfaces was bright and the other coated: when the heated disc was so placed between the thermometric discs that the blackened surface of the one opposed the metallic surface of the other, and *vice versâ*, no effect was produced upon the thermometer; but when the similar surfaces were opposed, namely, black to black, and metal to metal, the thermometer immediately indicated a great access of heat. In the first position the respective actions of the surfaces exactly balanced each other: in the second the good radiator was opposed to the good receiver, and the two bright surfaces to each other, so that everything favoured the effect on one side and opposed it on the other, and hence the great effect upon the thermometer.

It will be observed that these effects of radiation are singularly opposed to the *conducting* powers of the respective surfaces. If we touch the clean part of the canister it burns us; but we may place the finger with impunity upon the paper or flannel, which, though a good *radiator*, is a comparatively bad *conductor* of heat.

The following table of the comparative radiating powers of different substances, is drawn up from Leslie's experiments:—

Lampblack	100	Tarnished lead	45
Sealing-wax	95	Clean lead	19
Writing-paper	98	Polished iron	15
Crown glass	90	Tin plate)	
China ink	88	Gold	Polished . . . 12
Red-lead	80	Silver	
Isinglass	80	Copper)	
Plumbago	75		

It appears therefore that those surfaces which are not metallic, such as soot, paper, glass, &c., are much better radiators of heat than tarnished metals, lead, or iron; and that these latter radiate better than the polished metals, which consequently stand at the bottom of the list. It will also be recollected that the above numbers represent the *receptive* as well as the radiating powers of the respective surfaces. In regard to roughened metallic surfaces, Leslie found their radiating powers much dependent upon the manner in which they had been scratched; when a number of lines were scratched in one direction upon a bright metal, the force of ra-

diation was increased: he then drew the same number of lines, but so that they crossed each other at right angles, and a still greater radiant power was obtained; as if it depended upon the number of points produced.

The different radiating powers of metallic surfaces is stated by Melloni to be connected with differences in their densities. He formed two silver vessels, one of well hammered plate, the other of cast and slowly cooled metal; one side of each was highly polished, and the other scratched with emery-paper in one direction only. On filling them with hot water, he found the following differences:—

Hammered metal polished	= 10°	Cast metal, polished	= 13°·7
Ditto scratched	= 18°	Ditto, scratched	= 11°·3

The polished surface, therefore, of the cast metal, radiated much better than that of the forged, showing the superiority of inferior density; but with the scratched surfaces, the radiation is in favour of the hammered or denser metal, an effect which Melloni refers to the compression of its surface by the friction of the emery.

Let us now look at some of the economical applications of the facts arising out of the philosophy of radiation.

Before much was known respecting the radiating, and consequent cooling power of different surfaces, it was presumed that vessels of earthenware or porcelain were better calculated to retain heat, than those of metal; it was rightly argued, that the latter were by far the best *conductors* of heat, and it was inferred, therefore, that they would lose heat to the surrounding air more rapidly than bad conductors. Experienced tea-makers, however, always maintained that the best tea was made in a bright silver vessel, and that earthen teapots were of far inferior power; the former were said to *draw* much better than the latter. This opinion we now know is correct, and the obvious reason for the preference is, that the water retains its heat longer in the metal than in the porcelain vessel, and consequently extracts the soluble matter of the tea-leaves more completely.

“Vessels,” says Sir H. Davy, “that are intended to *retain* their heat, should be metallic, and highly polished; and, independent of elegance and delicacy, there is a reason, obvious from the preceding facts, why metallic vessels for the purposes of the table should be kept as bright as possible. Steam or air pipes for warming houses, should be polished in those parts where the heat is not required to be communicated, and covered with some radiating substance, such as lampblack or plumbago, in those rooms which are to be heated by them. Culinary implements should be blackened, and not polished, on those parts which are to *receive* heat. The heated surfaces of fire-places or stoves should not be metallic, but of stony or earthy materials; and in this case, much more heat will be communicated by radiation.”

It is also obvious, that whenever radiant heat is to be absorbed, rough, unmetallic surfaces should be employed; and these, in the case of solar rays, may be blackened, in order to render the heat more intense. Brick-walls are excellent absorbers and radiators of heat, and when exposed to the sun's rays they become very hot; afterwards, when the sun goes off, they again radiate the heat which they had previously received, and which

caused their excess of temperature over the surrounding bodies. Walls against which fruit-trees are planted are sometimes painted black, in order to get the highest possible degree of heat during their exposure to the sun; but it is not found that the fruit is thus improved.

The way in which we receive heat from our ordinary fire-places will now be intelligible, and it will be evident that it is principally by *radiation*, the hot and dilated air making its escape up the chimney, attended by an enormous waste of heat, and consequently also of fuel. The heat which radiates from the glowing coals, and from the heated surfaces about the grate, is projected into the chamber, traversing the air without heating it, and impinging upon the different bodies around, is received by them with different degrees of facility, dependent upon the nature of their surfaces: the carpet, and all similar surfaces, absorb the radiant heat with facility; furniture and wooden articles become also heated; and these radiate in their turn, and throw off their excess of heat above that of surrounding bodies. They also warm and dilate the air in contact with them, and thus the heat becomes more or less equally diffused throughout the chamber. Our clothes are also, in general, good absorbers of heat; so is the skin or cuticle; and by the absorption of the radiant heat we get warm on standing before the fire, at least upon that side or part which is exposed to it. This partial reception of heat by which we are burned on one side, while the other may be very cold, is one of the great objections to our common mode of warming apartments; and another is, that in winter, one part of the room only is comfortable, whilst others are disagreeably cold. In rooms heated by throwing into them a current of warm air, such inconveniences are not experienced; but then, unless there is at the same time a thorough ventilation, they produce a sensation of closeness which is unpleasant to those accustomed to open chimneys and fires. A combination of the two systems is the most efficacious and pleasant; warm air, properly and judiciously admitted at the parts of the room furthest from the fire; and an open grate, to assist in warming, and to accomplish a perfect ventilation. Grates or stoves have lately been contrived in which there is an open fire as usual, and which also throw out a stream of warm air, heated by being made to pass from below upwards through a double casing, surrounding all the heated parts of the grate; these stoves, when properly made and applied, are extremely effective and economical.

But it is seldom recollected that all attempts to render any individual apartment in a house uniformly warm, will be frustrated, unless the mass of air in the halls and staircases is also heated; this is most effectually accomplished by a properly-constructed stove upon the basement story, and although the expense of such an arrangement is considerable at first, it will be found, if properly and judiciously made, to effect a material annual saving in fuel. Dr. Arnott's stoves are also excellently adapted to all these purposes. Whilst upon this subject I may be allowed to remark, that it is to be regretted that architects and builders in general are extremely inattentive to the methods of warming and ventilation, both as concerns dwelling-houses and public edifices.

From what has been elsewhere stated respecting the conducting and carrying powers of bodies, in respect to heat, and from the phenomena

of radiation, it is obvious that when a body is allowed to cool in the air, its heat will be carried away, first, by the absolute conducting power of the medium; secondly, by currents established in it, in consequence of change of density; and thirdly, by radiation; and that the separate influence of each of these causes must be considered. Supposing, however, a body to be placed in a *perfect vacuum*, its heat would be dissipated by radiation only; to determine, under these circumstances, the rate of cooling, an elaborate inquiry has been undertaken by MM. Dulong and Petit (*Ann. de Chim. et Phys.*, vii.); but the details rather belong to physical than chemical science. It appears that bodies cool about twice as fast in the air as in vacuo: Dr. Franklin conceived that a body requiring five minutes in vacuo, would cool through the same number of degrees in air in two minutes. Count Rumford gives the proportions of five minutes and three. But the rate of cooling will much depend upon the relative temperature of the body, and it will lose unequal quantities of heat in equal times, forming, according to Newton, a decreasing geometrical progression. Thus, supposing the temperature of a body to be 1000° above the surrounding medium, and that it were to lose 100° of heat in the first minute, it would lose 1-10th of the remaining 900° in the second minute, (or 90°), and 1-10th of the residual 810° (or 81°) during the third minute, and so on; so that the number of degrees lost during the first five minutes, would be 100, 90, 81, 72.9, and 65.6. This law of cooling, however, though perhaps tolerably correct at low temperatures, becomes liable to much error at high ones, the error increasing as the temperature augments.

In relation to this subject, the following summary is given by Dr. Thomson, founded upon the researches of Dulong and Petit.

1. "When a body cools in a vacuum, the heat which it loses is entirely by radiation. When it cools in air, the process goes on more rapidly, because the quantity of heat radiated is the same as in vacuo, while an additional quantity of heat is conducted away by the air. 2. The rate of cooling of a liquid is not altered by the size or shape of the vessel. 3. The velocity of cooling of a thermometer in vacuo, for a constant excess of temperature, increases in a geometrical progression, when the temperature of the surrounding medium increases in an arithmetical progression. The ratio of this geometrical progression is the same, whatever be the excess of temperature considered. The truth of this law will be evident from the following table:—

Excess of temp. of the therm. centigr.	Velocity of cooling Water at 0° .	Ditto Water at 20° .	Ditto Water at 40° .	Ditto Water at 60° .	Ditto Water at 80° .
240°	10.69	12.40	14.35	—	—
220	8.31	10.41	11.98	—	—
200	7.40	8.58	10.01	11.64	13.45
180	6.10	7.04	8.20	9.55	11.05
160	4.89	5.67	6.61	7.68	8.95
140	3.88	4.57	5.32	6.14	7.19
100	3.02	3.56	4.15	4.84	5.64
120	2.30	2.74	3.16	3.68	4.29
80	1.74	1.99	2.30	2.73	3.18
60	—	1.40	1.62	1.88	2.17

"If we compare the five last columns of this table with each other, we shall find that the mean ratio is 1.161. In general, this geometrical progression requires to be diminished by a constant quantity, in consequence of the heat radiated back to the hot body from the walls of the vessel in which it is cooling. 4. When a body cools in vacuo, the time of cooling is materially influenced by the nature of the surface of the hot body; those bodies cooling soonest which radiate best. But this difference does not affect the law of cooling in vacuo. 5. When a body cools in any gas, the same portion of its heat is carried off by radiation that would be dissipated if it were cooling in a vacuum. Another portion is conducted off by the gas. This last portion is not affected by the nature of the surface of the hot body. It depends upon the conducting power of the different gases. 6. The celerity with which heat is communicated from hotter bodies to colder ones, when all other things are equal, is proportional to the extent of contact and closeness of communication between the bodies."—(Outline &c., § IV.)

§ 18.—PHOSPHORESCENCE.

THIS term is generally applied to those bodies which shine in the dark, without undergoing combustion, though, in some cases, a low form of combustion goes on at common temperatures, or when substances are only slightly heated, which has occasionally been confounded with the luminosity of phosphorescence.—(See a report upon this subject, by Dr. C. Williams, in the *Proceedings of the British Association*, iv. 588.) The products of *combustion* (properly so called), at different temperatures, will be noticed in the sequel. The varieties of *phosphorescence* may be considered under the following heads:—

1. Bodies which become luminous after having been exposed to light, and which are generally called *solar phosphori*.
2. Bodies which become luminous when moderately heated.
3. Bodies of vegetable and animal origin, which are spontaneously luminous at common temperatures.

1. SOLAR PHOSPHORI.—The attention of philosophers was first drawn to this curious subject, by an accidental discovery of Vincenzo Cascariolo, a shoemaker of Bologna, who (about the year 1630), being engaged in some alchemical experiments, had occasion to calcine a quantity of a species of native *sulphate of baryta*, found near Bologna, at Monte Paterno (*AIKIN'S Dictionary*, Art. PHOSPHORI). He observed that, whenever the spar had been sufficiently heated, it acquired the property of shining in the dark after having been exposed to the sun's rays, and that it would even continue thus to emit light for some hours. In consequence of this discovery, the Bolognian spar came into great request among the curious; and the best mode of preparing the *Bolognian phosphorus*, as it was called, became a subject of no small pecuniary importance. The most successful preparers of it were a family of the name of Zagoni, who continued to supply large quantities of it to the curious throughout Europe, and retained their monopoly for many years. Their process is not exactly known; but if the spar be powdered, and made into thin cakes, with mucilage of gum tragacanth, and then carefully calcined

in the open fire, and suffered to cool slowly, they will be found to answer the purpose: that is, they will glow for some time in a dark room, after having been exposed to a bright sunshine. Some management, which can only be learned by practice, is requisite in conducting the calcination. Any variety of sulphate of baryta will answer for the above preparation, but that which is massive, nearly opaque, and of a lamellar fracture, appears, on the whole, to furnish the most luminous product.

There are many other substances possessed of properties analogous to those just described. For the discovery of one of these we are indebted to Canton, by whose name it is usually known. *Canton's phosphorus* is made by calcining oyster-shells in the open fire for half an hour; after which the whitest and largest pieces are selected, mixed with about one-third their weight of flowers of sulphur, pressed into a crucible with a closely luted cover, and heated red-hot for an hour. When the crucible has become quite cold, turn out its contents, and select the whitest pieces for use.

For the following solar phosphorus, we are indebted to Mr. B. Wilson (*On Phosphori*, p. 20):—"Select a score of oyster-shells, the thicker they are the better; then take most of the flaming coals, but not all of them, off a fire that is burning briskly, strew the shells over the surface, and replace the coals that have been taken off. In about an hour's time take out the calcined shells, observing to break them as little as possible; and after exposing them for a few minutes to the light, they will be found to have acquired a high degree of phosphorescence, glowing in the dark in a very beautiful manner, with most of the prismatic colours. It is not, however, absolutely necessary that the shells should be calcined in the open fire, for if they are heated sufficiently in a close crucible, they will exhibit prismatic colours, chiefly blue and green, though not so bright as by the former method. If the calcination is effected in an iron crucible, all those parts of the shells that have been in contact with the sides of the crucible will glow with a red light. The contact of inflammable matter, and particularly charcoal, with the shells during their calcination, appears eminently to contribute to the brilliancy of the phosphorus. Hence it is that if the shells are calcined in a crucible, in contact with thin plates of steel, (steel being a compound of iron and charcoal,) the phosphorus thus produced will be much more bright, and of more various colours than when plates of iron are employed; and, on the other hand, if flat pieces of charcoal are made use of, the intensity of the colours, especially of the blue, green, and red, is far greater than in those produced by the steel."

Another solar phosphorus is that discovered by Baldwin. It is made by saturating diluted nitric acid with chalk, and evaporating to dryness, by which a *nitrate of lime* is obtained. This, when melted at a dull red heat, cools into a compact mass, which has the property of imbibing and emitting light.

It has been observed, in regard to these *solar phosphori* in general, that their luminous power is diminished by cold and increased by heat; that they are more brilliant in dry and warm than in wet and cold weather; that they shine most intensely after exposure to direct sunshine; but that some of them, especially the oyster-shells, exhibit their

phosphorescence when carried into a dark place, after mere exposure to ordinary daylight. It is sometimes said, that they absorb the same coloured light as that to which they are exposed, and that, if exposed to red light, they give out red, to green, green light, and so on; but this appears to be a mistake, the colours of the light being white or reddish white, and often prismatic, but independent of the colours of the rays to which they have been exposed. Moonlight is quite inadequate to render these bodies luminous; but the flash of gunpowder, the light of a bright candle or lamp, or of an electric explosion, suffices to make them shine more or less intensely.

The above are the most remarkable solar phosphori, but there are several other substances possessed of very similar properties, such as some diamonds, rock-crystal with its surface roughened, certain saline bodies, and writing-paper: these, however, are less powerfully luminous, and require good management to be observed. They should be brought out of the light to the observer, who should be stationed in a small closet, painted black on the inside, and with a black curtain hung up before the door. (BECCARIA, *Acta Bologn.*, 1744—1747, and *Phil. Trans.*, Lxi. 212. See also HEINRICH, *Bib. Univ.*, xv. 247.)

2. PHOSPHORI FROM HEAT.—There are many substances which become luminous when moderately heated; that is, at a temperature below a red heat. These differ from the preceding in the circumstance, that, after having been kept at any particular temperature till their luminousness is exhausted, they are incapable of shining again, except at a temperature greater than that to which they were first subjected. The substances belonging to this class are extremely numerous, and an extended series of experiments upon them, by Sir D. Brewster, will be found in the *Edinburgh Philosophical Journal*, I.; but there are only a few which are eminently luminous; of these the compact *phosphate of lime*, found native near Estramadura, in Spain; and certain kinds of *fluor*, or Derbyshire spar, especially the dark blue and slightly fetid variety, are the most remarkable: the former exhibits a beautiful pale-green light, intense enough to be seen in the daytime; and the latter shines with a purple tint; a variety termed, from its shining with a green light, *Chlorophane*, is particularly brilliant and beautiful. The best way of exhibiting them is to heat them in a dark room, in a spoon of platinum, over a spirit-lamp, the light of which is not sufficient materially to interfere with the observance of their phosphorescence. They should be in small fragments, but not too finely powdered. The *fetid carbonate of lime*, called *swinestone*, not uncommon near Bristol, several varieties of *calcareous spar*, and of *heavy spar*, and *powdered quartz*, are substances which are also luminous when heated; they may be strewed for this purpose upon a piece of iron which has been heated red-hot, and just ceased to glow. Mr. Pearsall has shown that, after the luminosity of many of these substances has been destroyed by heat, it may be restored to a certain extent by electrical discharges; and that electricity generally exalts the power, and in some cases confers it where it did not previously exist. Several other curious facts, in reference to this subject, will be found in his papers. (*Roy. Inst. Jour.*, i. 77 and 267.)

The substances which are phosphorescent by heat are also generally

so by *friction*, which is another productive source of luminosity. There are also several bodies which are rendered luminous by passing an electric shock through or over them; such, for instance, as a lump of loaf-sugar, which shines for several seconds afterwards with a beautiful blue light. (SKRIMSHIRE in *Nicholson's Jour.*, xv., xvi., and xix.)

3. SPONTANEOUSLY PHOSPHORESCENT SUBSTANCES.—Under this head we may place a variety of *animal substances* which, under certain circumstances, emit light. The flesh of certain fresh and salt water fish becomes luminous previously to its putrefaction; of these the tench and carp, and the herring and sole, are perhaps the most remarkable; the fish should be gutted and split, and the scales scraped off; if placed in a dark cellar, they are then often observed to shine within twelve or twenty-four hours, the time depending upon the temperature and state of the atmosphere, and probably other causes which have not been determined: this appearance ensues before any bad odour is perceptibly exhaled; and soles are often luminous in the dark, when perfectly fit for the table. Lobsters and crabs, under similar circumstances, are often very rich in phosphorescent matter. It appears, from the experiments of Canton and of Dr. Hulme (*Phil. Trans.*, vols. lix., xc., and xci.), that sea-fish become luminous in about twelve hours after death, that it increases till putrefaction is evident, and that it then decreases. Immersion in sea-water does not effect this luminous matter; on the contrary, the brine is itself rendered luminous: but it is extinguished by pure water, and by a variety of substances which act chemically upon the animal matter. The ligamentous parts are more luminous than muscular fibre; especially the eyes. Phosphorescence is rarely observed in the flesh of quadrupeds, and never in that of birds, under any circumstances of decomposition.

There are many *living animals* which have various powers of emitting light. One of these is the *glow-worm*; and there are others which, under certain circumstances, are powerfully phosphorescent. The common *hundred-legged worm*, found under bricks and pots in the garden, exhibits brilliant flashes of light when irritated. The *lantern* and *fire-flies* of warmer climates are also remarkable for their emission of light.

Dr. Macculloch, in his work on the Western Islands of Scotland, and in a paper published in the *Quarterly Journal* (xi. 249), has detailed some valuable facts respecting that beautiful appearance of light in sea-water, so well known to those who are conversant with the ocean during the darkness of night; he has shown that the sea is often crowded with worms and insects nearly invisible, and that its luminous property not only bears a relation to the existence and number of these at any time, but may generally be traced to the individuals by which it is caused. One of these luminous animals, described by Captain Home, is figured in the *Quarterly Journal*. N. S., vol. iv., p. 383.

In the *vegetable world* phosphorescence is a less common quality. *Decayed wood*, and occasionally *peat*, have been observed to emit a faint light; and there are a few flowers, among which may be mentioned the *tuberose*, *nasturtium*, and *marigold* (*Tropæolum majus*, and *Calendula vulgaris*), which have occasionally been observed to give out brilliant flashes upon a warm summer's evening. The leaves of the *Phytolacca decandra*, have also been seen to emit light, and a similar appearance

is mentioned by Mr. Mornay, peculiar to the sap of a Brazilian *Euphorbia*. There are certain mosses too, which occasionally phosphoresce; and some species of *Rhizomorpha* have been observed to be luminous in mines.

Certain substances emit light during crystallization: this has been occasionally observed with sulphate of potassa, but the phenomenon, according to H. Rose (*Ann. de. Chem. et Phys.*, lxi. 288), is most distinctly observed during the crystallization of arsenious acid from its solution in hydrochloric acid. About an ounce of the vitreous acid (not the opaque or pulverulous) should be dissolved in three ounces of the acid, diluted by an ounce of water; it should be boiled for about a quarter of an hour, and then suffered to cool very slowly, which is best effected by gradually diminishing the flame of the spirit-lamp used for heating it; in a dark place each crystal that is formed produces a spark of light, and on shaking the flask many crystals are often suddenly deposited, attended by vivid flashes.

We have now enumerated some of the leading cases of what is properly called *phosphorescence*; it appears to consist in an emission of light, independent of ignition or combustion, and referable to a variety of causes, none of which have been very satisfactorily investigated or explained. There are numerous other cases of luminosity referable to changes in the *electric states* of bodies, and which will afterwards be noticed in detail.

§ 19.—EFFECTS OF RADIATION IN NATURE.

THE earth, part of the surface of which is daily exposed to the action of the solar beams, will absorb the rays with various degrees of facility depending upon the nature of the surface; and during the night it will again radiate, or throw off a portion of the heat it has so acquired. It has been ascertained that the extent to which this diminution of temperature takes place, is greatly dependent upon the aspect of the sky; when the night is clear, and the heavens cloudless, it goes on more rapidly, and to a much greater extent, than when the sky is overcast and cloudy; and hence it is, that upon clear nights there is a much greater deposition of dew than in cloudy weather. To understand this, it must be recollected, that *dew* is not a kind of fine rain showering down upon the earth from above, but that it depends upon the deposition of moisture contained in the state of vapour in the air, and is, in its formation, precisely similar to what happens when a glass of iced water is brought into a warm room in summer; the coldness of its surface abstracts the heat from the vapour in the air, and causes its condensation in the form of water, which is deposited exactly like dew upon the outside of the vessel*. So the earth, upon a fine cloudless night, accord-

* This is also the reason why thick and substantial walls in the interior of houses become damp, and often very wet, in certain states and changes of weather. They are so massive as to retain an acquired temperature for a long time, and during a winter's frost become

cold throughout; upon a sudden thaw attended by a very humid state of atmosphere, the vapour or moisture of the air is condensed in the liquid state upon these cold surfaces, because they abstract its heat, and consequently cause it to run down in the form of water.

ing to some, in consequence of the accelerated radiation of its own heat, and to others, in consequence of the radiation of cold from above, becomes colder considerably than the superincumbent atmosphere, and therefore the aqueous vapour, more or less of which is always contained in the air, is condensed in the liquid form upon the surface of the ground; and, of course, most abundantly, upon those parts of the surface, which being the best radiators, or receivers of radiant matter, have their temperatures most depressed. Thus, walking in the garden upon a bright autumnal morning, after a clear night, we observe the dew very unequally deposited: it is commonly most abundant upon the grass-plats, for mown grass is an excellent radiator; it becomes, therefore, colder than the adjacent gravel-walks, upon which the dew is less abundant. If we place a thermometer upon the grass, and another upon the gravel, we shall find the former sink several degrees below the latter; and under circumstances favourable to the deposition of the dew, the earth's surface will always be found colder than the air above it. A thermometer on the grass has been observed, under favourable circumstances, to fall as much as from twenty to thirty degrees below one suspended some feet above it. The consequence is, that the lower strata of the atmosphere in contact with the cold surface of the earth, are considerably colder than the higher parts; and if the air is tranquil, will remain so for some time, especially in *hollows*, and other places protected from currents, and where the warm and the cold air are not therefore mixed by mechanical agitation. Hence it is that delicate plants often suffer more in situations apparently protected, than in those which are open and exposed, and where the cold air has not such a chance of lying quiet upon the surface.

All *good radiators*, exposed upon the earth's surface, will become *colder* than bad ones; if, therefore, we place upon an exposed gravel-walk a piece of flannel and a piece of tin-foil, the former will have abundance of dew thrown down upon it, and the latter none; and, in reference to this fact, it is curious to observe the influence of the natural textures and surfaces of foliage. Smooth, varnished leaves, have no dew deposited upon them, under circumstances in which there is an abundant deposition upon rough and downy leaves; the former, therefore, seldom suffer from this cause of cold, but the latter are often frost-nipped.

The remarkable influence of clouds in preventing radiation, seems first to have been noticed by Dr. Wells, whose *Essay on Dew* deserves the attentive perusal of all who are interested in this part of meteorology. He found that, if the night, at first clear, becomes cloudy, the temperature of the grass always rises, independent of any changes of calmness, and nearly so of change of atmospheric temperature. Upon one such night the grass, after having been *twelve* degrees colder than the air, became only *two* degrees colder, the temperature of the atmosphere remaining stationary; and, on another occasion, the temperature of the grass rose *fifteen* degrees, while the air only sustained an increase of *three and a half*. Any protection interposed between the earth and sky, prevents radiation, in the same way as a cloud. If we place four poles in the ground, and stretch a mat or canvass upon them, the plot underneath will be effectually preserved from those changes of temperature referable to the escape of radiant heat from the surface, or, to the reception of radiant

cold from above. In this way gardeners protect young and tender plants; though it is obvious that any general changes, dependent merely upon atmospheric temperature, would not be interfered with, nor the cold kept off by such a contrivance.

Radiation, therefore, is constantly going on from the earth towards the regions above. If we place the bulb of a delicate thermometer, especially if it be covered with some good radiating substance, in the focus of a concave metallic mirror turned towards the clear sky, it will indicate cold: this was referred by Leslie to radiation of cold from the regions of space; and thus he employed a differential air-thermometer in the construction of his *Æthrioscope* (See *Encyc. Brit.*, Art. CLIMATE,) to indicate, as he terms it, "*cold pulses emanating from the sky*," or, as others have expressed it, to give a comparative idea of radiation proceeding from the surface of the earth towards the region of perpetual congelation in the atmosphere. "The thermometer is protected by its position from the radiation of surrounding objects, and its own radiant heat is projected towards the clear space, or falling upon the concave surface of the mirror, is reflected in parallel lines in the same direction. This effect is produced even while the sun is above the horizon, provided the mirror be turned from the direct rays of that luminary; and at night a depression of 17° below the temperature of the air and surrounding objects may commonly be produced. Perfect stillness of the atmosphere is necessary, and perfect transparency also, for otherwise the balance of temperature is soon restored by convection, and the slightest mist destroys the effect by a counter-radiation." DANIELL, § 275.

In the eighty-third volume of the *Philosophical Transactions*, Mr. Williams has described the mode of obtaining ice in Bengal, where the atmospheric temperature never falls to the freezing-point. It is evidently chiefly effected by radiation from the surface of shallow pans of water (and water is an excellent radiator), which are placed upon dry stubble in open situations: calm, serene, and cloudless nights are most favourable to the purpose; and thin crusts of ice are thus frequently obtained. In such cases the production of cold has sometimes been referred to evaporation, but that this is not the cause of the diminution of temperature, in the present instance, is proved by the peculiar circumstances requisite for the success of the operation being entirely independent of it.

§ 20.—OF IGNITION AND COMBUSTION.

It will be evident, from the contents of the few preceding pages, that there is a connexion between light and heat, and that they are mutually disposed to produce each other; indeed, they are probably convertible into each other; but these, and other mysterious relations between them are as yet very imperfectly understood.

In the mean time it may be right to mention a supposed exception to the relationship between heat and light, furnished by an examination of the *lunar rays*, which, though concentrated by the most powerful lenses, are incapable of affecting very delicate thermometers. De la Hire collected the rays of the full moon when in the meridian, by a lens thirty-five inches in diameter, and threw them upon the bulb of a very sensible

air-thermometer, but they produced no effect, though they were thus concentrated 306 times. It is not, however, surprising that the moon-beam should be thus inefficient, when we consider the extreme feebleness of its illuminating power, as compared with a solar ray of the same size; the light of the latter being at least 300,000 times greater than that of the former. It appears probable, therefore, that the properties of the moon-beam are to be referred to its *feebleness*, as compared with that of the sun, though there may be some peculiarity in its nature, or some power in the surface of the moon of retaining the heat, whilst it emits the light received from the sun. It has even been supposed that the moon may radiate cold.

By the terms *ignition*, and *incandescence*, we express a property which bodies possess of giving out light, whenever their temperatures are raised up to a certain high point. The quantity of light thus emitted increases with their temperature: at first it is dim and feeble; then it becomes dingy red, and the bodies are said to be *red-hot*; then bright red, commonly called a *cherry-red* heat; then, as the temperature increases, the body becomes of an *orange* or yellow tint, and at length acquires such brilliancy as to be painful to the eye; the latter is usually termed *white heat*.

Various experiments have been instituted to determine the temperature at which bodies become visibly red-hot; this, in a dark place, certainly exceeds six hundred and sixty degrees of Fahrenheit's scale, for at that temperature mercury boils, and it is not, in the least degree, luminous. Sir H. Davy's experiments place the degree of incipient luminosity in a dark place at about 810° . A dull red, visible in daylight, is probably equal to about 1000° , a full red heat to 1200° , an *orange heat* to 1700° , and a white heat to 3000° .

These observations of course only apply to bodies capable of sustaining high temperatures without changing their state, or undergoing decomposition, most substances being either dissipated or destroyed before they attain the requisite temperature for ignition; or, if heated in the air, *inflaming* and undergoing *combustion*.

In all the ordinary cases of combustion air is present, and the phenomena presented by the burning body are referable to the chemical action which ensues, at high temperatures, between it and one of the component parts of the air, called *oxygen*, which, being invisible, long escaped observation as an important agent in the process, and of which we shall have to speak at length hereafter.

The *temperatures* at which bodies burn or inflame in the air are extremely various; some take fire under all circumstances the moment they are exposed to it; others require their temperatures to be more or less elevated; and some refuse to burn under any circumstances. Thus we speak of *combustible* and *incombustible*, or *inflammable* and *uninflammable* bodies; and we call the oxygen of the atmosphere, and such other bodies as are possessed of similar powers, *supporters of combustion*. All common cases of combustion, then, taking place in the atmosphere, depend upon the union of the combustible with oxygen; between these bodies there necessarily exists a strong chemical attraction, and of this, one of the results is the *evolution of heat and light*.

The result of the union of the combustible with the supporter, is called the *product of combustion*; it is very commonly gas or vapour, and eludes ordinary observation: thus, the immense quantity of coal daily consumed as common fuel, combines with the oxygen of the air, and forms several products, of which the principal are *carbonic acid gas* and *steam*; and these pass off by the chimney, and are dissipated in an invisible state through the immense mass of the atmosphere. The *incombustible* earthy matter contained in the coal resists combustion, and forms *ashes*; or, mixing with a part of the coal, renders it difficult of combustion, as we see in *cinders*.

But the product of combustion is often a *solid* body; thus, if we throw a piece of the metal *zinc* into the fire, or heat it red-hot in a crucible, it burns with a very vivid flame, and a quantity of a solid white substance is produced, which is a compound of the metal and the oxygen of the air, and is, therefore, called *oxide of zinc*.

Nothing is more common than to speak of the *destruction* of bodies by combustion; but the term is in so far improper, inasmuch as *matter is indestructible*; and when we seem to destroy a coal by burning it, we, in fact, only cause it to enter into new combinations; and the carbon which it chiefly consists of, although it apparently disappears, has only entered into a new combination, which may be found escaping from the chimney in the invisible state of air or gas, but from which the solid carbon may again be obtained by certain chemical operations.

Such are the general results of combustion: they have here been adverted to in order to explain the nature of *flame*, a subject which has been studied with much attention and curious results by several eminent chemists.

It has often been doubted whether pure gaseous matter is, under any circumstances, susceptible of becoming luminous; certain it is, that its temperature may be elevated far beyond that which is required to ignite solid bodies, and it yet remains invisible. By passing air over heated surfaces, its temperature has been so far elevated as to render metallic wires red-hot, yet was the air itself not at all luminous. Of this a good instance is afforded by the air that issues from the lamp-glass of an Argand gas-burner, which, though not luminous, will heat a fine wire red, or even white hot, held some inches above it. *Flame*, however, may, in general, be regarded as *luminous gaseous matter*, and its *temperature* is under certain circumstances very intense, even where the *light* which it emits is excessively feeble. Perhaps the purest form of flame which we can exhibit is that of hydrogen gas; its *light* is so feeble as scarcely to be visible in broad daylight; yet its *temperature* is very high, as may be shown by holding a fine platinum wire in it, which immediately becomes *white-hot*: the other metals, under similar circumstances, are generally melted or burned.

Upon what, then, does the *luminosity* of a flame, which renders it valuable as a source of artificial light, depend? *Principally upon solid matter diffused through it, and ignited by it*. In the experiment just cited, the flame of the hydrogen is rendered luminous by the wire; and if we blow any substance through it in fine dust, its brightness will be proportionately increased, though the solid matter be not itself inflam-

mable; as, for instance, if we sift a little lime or magnesia into or through it.

The extent to which the light may be increased is also well illustrated by the ignition of lime in the oxyhydrogen blowpipe, as suggested by Drummond (*Phil. Trans.*, 1826, p. 324), and as since used for the illumination of the solar microscope. That it is the vapour of the lime, raised to this high temperature, that occasions the intensity of the light, is shown by the roof of the lantern being covered by a sublimate of lime. There can be little doubt that the brilliancy of the voltaic discharge between points of charcoal is partly referable also to the formation and ignition of volatilized carbon. There are few instances of a more luminous flame than that of phosphorus, in which the great evolution of light depends upon the ignition of the produced phosphoric acid; and if this acid (forming the smoke of phosphorus) be led by a tube into the flames of alcohol or of hydrogen, it greatly increases their luminosity.

In the flame of tallow, wax, oil, and coal-gas, the brilliancy of the light is chiefly owing to very finely-divided charcoal, which is blended with, and burned in, the flame, and which, if in too large quantity, causes the flame to smoke, as we see especially in ill-made tallow-candles, which, notwithstanding frequent snuffing, throw off a quantity of soot into the surrounding atmosphere, creating a disagreeable suffocating smell, and blackening the walls and ceilings of our apartments*.

Such, then, appears to be the source of the *light* of flames; but there are some other curious particulars respecting their construction, which require more full explanation. In a common candle, the wax or tallow is drawn into the burning wick by capillary attraction, and is there converted into vapour, which ascends in the form of a conical column, and has its temperature sufficiently elevated to cause it to combine with the oxygen of the surrounding atmosphere with a temperature equivalent to a white heat. But this combustion is *superficial* only, the flame being a thin film of white-hot vapour, enclosing an interior portion, which cannot burn for want of oxygen. That this is the case is easily shown, by bringing down a piece of thin glass upon the flame of a candle, so as to cause a transverse section of the flame. We shall then observe a *ring of light* surrounding the interior dark part of the cone (fig. 96,) and the

* For all common purposes of illumination it is essential that the constitution of the light of flames should resemble that of the sun, and, like it, consist of a due admixture of the primary colours; it is seldom, however, that artificial light is perfect in this respect, and accordingly it is not suited to the correct and perfect display of colours, and when viewed through a prism generally shows a predominance of some one tint. The influence of light of *one colour* upon external objects is seen by viewing them through coloured glasses, or more perfectly by illuminating them by a *monochromatic flame*. We obtain an effect of this kind by a lamp fed with spirit

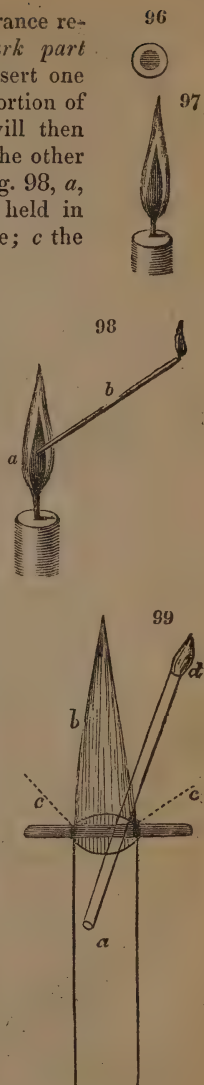
of wine burning in a wick impregnated with common salt, and which, as it produces little else than yellow light, has been called a *monochromatic-lamp*; it shows no perfect colour except yellow, and furnishes a curious analysis of such compound colours as contain yellow by converting them to that tint; all other colours appear very dingy, and nearly black. The brilliant red of cinnabar, as in sealing-wax, and of iodide of mercury appear pale yellow; that of cochineal, as in lake and red morocco, looks black; so also do the brilliant blues of smalt and ultramarine. See Sir D. BREWSTER'S *Letters on Natural Magic*, p. 107.

vertical section of the flame will put on an appearance resembling fig. 97. To prove that *the interior dark part consists of inflammable gaseous matter*, we may insert one end of a small glass tube into the dark central portion of the flame of a large candle, and the interior gas will then make its escape through it, and may be lighted at the other end of the tube, so as to form a second flame. Fig. 98, *a*, shows a section of the flame; *b* the glass tube held in an inclined position in the central part of the flame; *c* the inflammable gas kindled at its extremity.

It is in consequence of this structure of flame that we so materially increase its heat, by propelling a current of air through it by the *blowpipe*, or by supplying its interior with oxygen, as in the gas jet suggested by Mr. Daniell (*Phil. Mag.* 3rd series, II., 57). The perfection of the *Argand burner* is also referable to the same cause.

These peculiarities become more evident in larger flames; so if in a steady atmosphere we inflame some ether or alcohol in a small capsule, we may introduce phosphorus or gunpowder into the centre of it, and they will not be inflamed: a large jet of gas issuing from the top of a lamp glass, may, with a little management, be so inflamed as not to pass down to the orifice of the burner, and it then forms a hollow cone of flame; a small rod of wood, such as a pencil, or a piece of twisted paper, may then be placed across the flame, and it will only be charred or burned at the luminous surface, and not at all affected in the centre. *a* represents the lamp-glass, through which the current of gas is passing; *b* the cone of flame at its mouth; a piece of wood laid across it is singed at *c*; and by the tube, *d*, gas may be drawn out of the interior, and inflamed at its other extremity.

There are several substances which burn at lower temperatures than required for the production of flame. We often see the coals in a common fire glowing at a dull red heat, but not hot enough to inflame the smoke, or inflammable gas and vapour that passes over them, which however may be immediately effected by a piece of flaming paper, or by stirring the fire, which not only accelerates the combustion, but mixes air with the vapour, so as to render it more easily inflamed. The long-continued glowing of the wick of a green wax taper (coloured by verdigris) is another case of combustion, going on at a temperature below that of flame; so is the luminosity of a stick of phosphorus. The phenomena attendant upon such states of combustion are highly curious: when, for instance, spirit of wine is burned *with flame* in the usual way, carbonic acid and water are the products of its combustion; but when burned *without flame*, it pro-



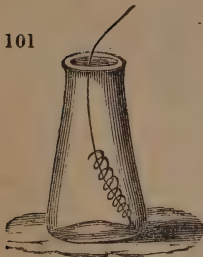
duces acetic acid. The mode of effecting this *slow combustion* is sufficiently simple. A small spiral coil of fine platinum wire is placed upon

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the wick of a spirit-lamp, and allowed to project about a fourth of an inch above it, as represented in fig. 100. The lamp is then lighted, and suffered to burn for a few seconds, when the flame is put out by an extinguisher, which, however, must be *instantaneously* removed. In this way the coil of wire retains heat enough to carry on the *slow combustion* of the alcoholic vapour, and it continues to glow with a red heat as long as spirit remains in the lamp, and to produce the peculiar acetic product just mentioned: in this way of proceeding, the heat never becomes intense enough to cause the inflammable vapour to burn with flame.

101



There is another, and a very instructive way of making a similar experiment, which consists in pouring a teaspoonful of ether into a tall ale-glass, or small jar of the form represented in fig. 101, and then suspending in it a coil of fine platinum wire, previously heated by holding it for a minute in the flame of a spirit-lamp. The wire being now immersed nearly red-hot into the mixture of atmospheric air and ethereal vapour, *glows with a red heat, causing the slow combustion of the vapour*. It often happens that a part of the wire becomes *white-hot*, and in that case *flame* is produced, and the ether burns with its usual products; but so long as the wire continues only red-hot, no inflammation ensues.

It follows, then, that *flame requires a very high temperature for its existence*; and, consequently, that if we can devise any mode of *cooling* it, it will be *extinguished*. A very small flame, for instance, is extinguished by bringing a large mass of iron near it, or by carefully surrounding it by a coil of wire; the metal abstracts its heat. But by far the most interesting experiments upon this subject are made by help of brass or iron wire-gauze, which may be obtained of different degrees of fineness, and with which the following illustrative experiments are easily shown.

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103



Procure a piece of this gauze about nine inches square, and of such fineness as to have about thirty meshes in the square inch: bring it gradually down upon the flame of a wax-candle, or, what answers better in all these cases, upon a jet of coal-gas, and the appearances represented in fig. 102 will be produced. The flame will be cut off where it touches the gauze, and we have a good opportunity of observing the exterior luminous circle described above (fig. 96.) In this case the inflammable matter of the flame (in the form of smoke) passes through the wire-gauze; but, in its passage, it is so far *cooled* as to be *extinguished*, and the *flame* is thus prevented from traversing

the wire-gauze. If we now bring a lighted taper above the flame, to the upper side of the wire-gauze, the gas or smoke will be kindled, and the flame continue to burn uninterruptedly, as in fig. 103.

If the meshes of the wire-gauze used in these experiments be not sufficiently small, or if the wire becomes intensely heated, the flame will pass in either instance; because the cooling power is in the one case prevented by the largeness of the apertures, and, in the other, by the high temperature of the wire; or, the wire-gauze may be held in a jet of uninflamed gas, and lighted upon its upper surface, in which case the flame burns there, but cannot descend through the gauze to kindle the gas at the orifice of the burner. This experiment may be curiously varied by placing a small piece of camphor in the centre of a piece of wire-gauze about a foot square, and applying a flame to its *lower* surface. The vapour of the camphor, which is very inflammable, burns with a bright flame upon the lower surface of the gauze, but cannot pass upwards through it, in consequence of its cooling power; so that the camphor itself lies upon the surface of the gauze, in an uninflamed state, though sufficiently heated to furnish inflammable vapour for the sustenance of the flame beneath.

The power of a metallic tissue thus to intercept or extinguish flame will depend upon the heat required to produce the combustion, as compared with that acquired by the tissue; and the flame of the most inflammable substances, and of those that produce most heat in combustion, will pass through a metallic tissue that will intercept the flame of less inflammable substances, or those that produce little heat in combustion: so that different flames will pass through at different degrees of temperature. The cooling power of the wire-gauze is referable to its excellent conducting power for heat; it also, by use, becomes a powerful radiator of heat.

These, and many other interesting investigations connected with the subject of flame, we owe to Sir H. Davy, who most ingeniously applied them in the construction of his *miners' safety-lamp*.

Coal-mines are often infested by a species of inflammable gas (carburetted hydrogen), known under the name of *fire-damp*, which, when mingled in certain proportions with atmospheric air, forms a mixture which explodes upon the contact of flame. Attempts had been made to light such mines so as to avoid explosion, but none were effectual; at length Sir H. Davy constructed a lamp upon the principles explained, which has been used with safety and success.

It is obvious, that if we place a lighted lamp or candle within a perfect cage of wire-gauze, no flame will be able to penetrate *from within* to the surrounding medium, in consequence of the cooling power of the metallic tissue. The annexed figure (104) represents a lamp constructed upon such principles. A is a cylinder of wire-gauze, with a double top, carefully fastened, by doubling over, to the brass rim B, which screws on to the lamp C. The whole is protected and rendered convenient for carrying, by the frame and ring D. If the



cylinder be of twilled wire-gauze, the wire should be at least of the thickness of one-fortieth of an inch, and of iron or copper, and 30 in the warp, and 16 or 18 in the weft to the square inch. If of plain wire-gauze, the wire should not be less than one-sixtieth of an inch in thickness, and from 28 to 30 both warp and woof.—(DAVY *on the Safety-lamp*, p. 114, *et seq.*)

The operation of this lamp may be shown by suspending in it a glass jar, and then admitting a sufficient stream of coal-gas to render the enclosed atmosphere explosive: or, what answers nearly as well, by immersing it into a jar, at the bottom of which is a little ether, and which supplies, by its vapour, an inflammable atmosphere. The flame of the lamp first enlarges, and is then extinguished, the whole of the cage being filled with a lambent blue light; on turning off the supply of gas, or gently blowing the ethereal vapour out of the vessel, this appearance gradually ceases, and the wick becomes rekindled when the atmosphere returns to its natural state.

As the *safety* of these lamps entirely depends upon the perfect state of the wire-gauze, and upon the non-existence of any aperture or channel sufficiently large to admit of the passage of flame, they should, when in use in a coal-mine, be inspected daily. In gas-manufactories, spirit-warehouses, and in all cases where inflammable vapours or gases are likely to be generated, as in the examination of foul sewers and drains, it is obvious that these lamps are importantly applicable*.

* It has been shown, that by throwing a strong jet of coal-gas and air, in explosive proportions, upon the wire-gauze of these lamps, the flame occasionally passes, and this circumstance has been urged as a new experiment, proving the inefficiency of Sir Humphry's safety-lamp: but all practical and unprejudiced experience shows, that when carefully attended to, and used with common caution (which unfortunately is not always the case), they are perfect and efficient safeguards. That Sir Humphry was aware of the possibility of causing the flame to pass is obvious from the following passages of his essay.

"Single iron wire-gauze of the kind used in the common miner's lamp, is impermeable to the flame of all currents of fire-damp, as long as it is not heated above

redness; but if the iron wire be made to burn, of course it can be no longer safe; and though such a circumstance can perhaps never happen in a colliery, yet it ought to be known and guarded against."

"If a workman, having only a common single lamp, finds the temperature of the wire increasing rapidly in an explosive mixture near a blower, he can easily diminish the heat by turning his back upon the current; and keeping it from playing upon the lamp, by means of his clothes or his body; or by bringing the lamp nearer the orifice from which the fire-damp issues, he may extinguish it: and there never can be any occasion for him to place his lamp in the exact point where two currents, one of fresh air and one of fire-damp, meet each other."

CHAPTER III.

CHEMICAL ATTRACTION, OR AFFINITY.

IN a former chapter we have considered *attraction* as disposing the *similar* particles of bodies to adhere, so as to form masses or *aggregates*; and, in many instances, to arrange themselves according to peculiar laws, and to assume regular geometrical figures. We then proceeded to show that *heat*, or *calorific repulsion*, was a power opposed to *aggregation*, tending to separate the particles of matter, and in many ways connected with those extraordinary phenomena which have been referred to *etherial matter*, and under which we were led to speak of *light* and *radiant heat*. We are now to give an outline of the extensive changes which result from certain attractive powers, appertaining to *dissimilar* particles of matter, and sometimes therefore called *heterogeneous*, in opposition to *homogeneous*, *attraction*: they are usually comprehended under the term *chemical affinity*.

§ 1.—GENERAL RESULTS OF CHEMICAL ATTRACTION.

A GOOD instance of *chemical attraction* is afforded by the mutual action of *copper* and *sulphur*. If 16 parts of sulphur broken into small fragments be mixed in a glass flask with 60 parts of copper filings, or turnings, no action ensues; they may be triturated together, but still remain a mere *mixture* of sulphur and copper; but, if heat be applied, so as to fuse and vaporise the sulphur, the copper presently begins to *combine* with it; heat and light are evolved, the copper glowing and burning in the sulphur vapour; and a brittle black compound, quite unlike sulphur or copper, namely, a *sulphuret of copper*, is the result. This simple experiment furnishes the following facts for consideration. First, it shows that mechanical aggregation is opposed in this case to chemical action, and that the sulphur and copper do not combine, till the aggregation of the former is diminished or overcome by heat. 2nd. That chemical action is here attended by the phenomena of combustion. 3rd. That the product has properties essentially different from those of its component parts. 4th. That sulphur and copper combine in certain proportions only; certain definite quantities of sulphur and copper being required to form the *sulphuret*.

We may first observe, that *chemical action is promoted by whatever tends to diminish aggregation or to disintegrate and separate the particles of matter*. In the preceding case, this is effected by *heat*; although it be true, as we shall afterwards find, that *electrical powers* may thus be exalted and called into action. It is this property or effect of heat, that renders it so essential an agent in many chemical operations, both upon the large and small scale.

Another mode of diminishing aggregation, and thereby promoting chemical action, is *solution*, the importance of which, as a prelude to the process of crystallization, has already been noticed (p. 110): its effects are shown by pouring water upon the mixture of tartaric acid and bicarbonate of soda, commonly termed *effervescent* or *sodaic powders*; the materials,

when dry, have no mutual action, but, when dissolved in water, the acid immediately decomposes the carbonate. Hence arose the old, though not perfectly correct, chemical axiom, "*Corpora non agunt nisi sint soluta.*"

But, in many instances, the mere diminution of aggregation by mechanical means, is effective in enabling substances to act chemically upon each other; thus, chlorine has little action upon a lump of metallic antimony, but *powdered* antimony thrown into the gas immediately burns, and produces a *chloride of antimony*: a piece of marble put into dilute hydrochloric acid, is only slowly acted on; but when the surface is increased, and the aggregation overcome by *pulverisation*, it is rapidly decomposed and dissolved. Lead, in its ordinary state, is scarcely acted upon by the air at common temperatures; but if the salt, called *tartrate of lead*, be heated red-hot, in a small tube or phial, the black matter which is obtained contains the *lead in a state of very minute mechanical division*, and in this state it takes fire upon exposure to air. There are some cases of chemical attraction, promoted apparently by peculiar states of the *surfaces* of bodies, which are of an extraordinary nature, and not easily explained: such are the action of certain porous bodies, and of perfectly clean, or finely divided (spongy) platinum upon certain gaseous mixtures: these we shall again refer to.

The evolution of heat and light, attending chemical action, is especially observed where the mutual affinities are intense, or where combination is rapid, and the electrical states of the acting bodies are eminently opposed. That it is not always explicable upon the theory of latent heat, or increase of density, is evident from the numerous cases of an opposite nature in which it occurs, as in the explosion of, for instance, fulminating mercury, and the expansion (attended by decomposition) of the oxide of chlorine. Nor does it appear that any one kind of matter is essential to *combustion*: it is a universal effect of intense chemical action, and proportionate to its rapidity: this is well illustrated in the *slow* and *rapid* combustion of phosphorus; the former exhibits a pale blue light, visible only in the dark, and attended by trifling elevation of temperature; the latter is brilliant in the extreme. When a candle burns, the substances of which it is composed are entering into chemical combination with the oxygen of the surrounding atmosphere; so also with respect to the coals consumed in our fires; and in both cases we observe the combustibles gradually losing their solid form, and acquiring an invisible æriform state; dissolving, as it were, in the air, and disappearing. If we apply a spark to a small heap of gunpowder, it is instantly dissipated in the gaseous form, and a bright flame ensues. In these cases it will always be remembered that there is no *destruction of matter*, but that the charcoal and other substances, composing the candle, the coal, and the gunpowder, have merely entered into new chemical arrangements, and are to be found, as we shall afterwards particularly show, in the *products of combustion*.

The next result of chemical action is, *the production of forms of matter possessed of properties entirely distinct from those of their component parts*, so that it is impossible to anticipate, from our knowledge of the characters of the latter, those which are to belong to the resulting com-

pound: hence chemistry is essentially a science of *experiment*. Oil of vitriol, for instance, or *sulphuric acid*, is a highly acrid and corrosive liquid, but it is composed of tasteless and comparatively inert elements, namely, oxygen, sulphur, and water. The elements, oxygen and nitrogen, which, in a state of *mechanical mixture*, constitute the air we breathe, give rise, when *chemically combined*, to one of the most active agents of the laboratory; namely, *nitric acid*. Again, if sulphuric or nitric acids be combined with caustic potassa, comparatively mild and inert *neutral salts* result, namely, the *sulphate* and the *nitrate of potassa*, in which none of the properties of the component acid and alkali can be recognised. In art, these remarkable changes are made subservient to the most important purposes. A variety of extremely useful compounds are obtained by the union of elements comparatively useless and unimportant; and, by the decomposition of apparently insignificant compounds, their more useful and important elements or components are separated. In nature, analogous changes are more strikingly presented to our observation, and the flower, the shrub, and the tree, are seen gradually to be formed and developed out of materials contributed by the air and soil, and in all respects most dissimilar to the new products of the vegetable: it is true that in these, and in analogous cases which might be taken from the animal kingdom, the mysterious power of vitality interposes; but such changes are nevertheless *chemical*, and legitimate objects of chemical inquiry.

There are many beautiful experiments illustrative of the total change of all obvious properties of substances as a consequence of chemical combination; as one striking instance, we may adduce the mutual action of *oxygen and nitrous gases*; these bodies are respectively permanently elastic fluids, without colour, taste, or smell: when mixed over water, they immediately enter into chemical combination, lose their elastic form, become of a deep orange colour, intensely sour, and of a peculiar odour; in their separate state they are insoluble in water, but the body which has resulted from their combination is perfectly soluble in that fluid.

Change of colour is a common, but also an important, result of chemical action. By exposure to light, air, and moisture, the greater number of colours are gradually destroyed, in consequence of the chemical agencies that ensue; a similar destruction of colour takes place more immediately upon the application of chlorine; and hence these agents are resorted to, to effect the purpose of *bleaching*. In the arts of *dyeing* and *calico-printing*, not only are fugitive colours rendered permanent, but their tints are variously modified, by chemical means. Of the vegetable blues, there are many which are rendered *red* by an acid, and *green* by an alkali; and hence paper stained with the juice of violets, or of the blue flag, or of the petals of the blue heart's-ease, is useful as a *test* of the presence of alkaline bodies. The same principle is applied to other purposes: if, for instance, an acid be gradually added to an alkaline solution, it is found that there are certain proportions in which they exactly *neutralize* each other; that is, a point at which the liquid neither exhibits acid nor alkaline characters. This point may be precisely learned by the above tests, for the solution then has no effect on the vegetable blue; but if either acid or alkali be predominant, that is, if the point of neutraliza-

tion has not been exactly attained, then the test, by the tint which it assumes, announces the predominant element: *green*, if alkaline, and *red*, if acid*.

In other cases, change of *colour* announces the presence of peculiar elements or compounds: thus ferrocyanide of potassium shows iron by a *blue* colour, copper by a *brown*, nickel by a very *pale green*, &c., and there are numberless other tests applicable upon the same principle.

Among the results of chemical action, we may next notice those which relate to the *change of state or form, sustained by the acting bodies*. When substances are burned in the air, they generally pass, as already observed, from the *solid* to the *aëriform* state; and the deflagration of gunpowder is a good instance of such sudden conversion; the converse change, that of *gases* into *solids*, is not so common, yet such cases are not unfrequent. When, for instance, ammonia and hydrochloric acid, both *gases*, are mixed, they immediately condense into a white salt, which is *hydrochlorate of ammonia*. When one part of fuming nitric acid is added to two of strong alcohol, the *liquids* presently disappear, with violent ebullition, in the form of an inflammable *vapour*; and when chlorine and carburetted hydrogen *gases* are mixed, they form a *liquid* of the appearance of oil.

Liquids by combination produce *solids*, and *solids* produce *liquids*. A strong solution of chloride of calcium, mixed with one of carbonate of potassa, soon concrete when shaken together. Excess of a strong solution of tartaric acid, added to strong liquid ammonia, solidify into *bitartrate of ammonia*, with the evolution of *heat*. A mixture of pure alcohol added to a saturated solution of sulphate of magnesia, congeals into a crystallized solid. Crystals of sulphate of soda, rubbed with an equal quantity of nitrate of ammonia, gradually form a liquid. So also the solid amalgams of lead and bismuth, when triturated together, assume a liquid form, and become *cold*.

§ 2.—THEORY OF COMBINATION AND DECOMPOSITION.

CHEMICAL affinity is frequently spoken of under the term *elective attraction*, and is said to be either *simple* or *complex*. It is sufficiently obvious that different bodies are possessed of different attractive powers: and, accordingly, if several be brought together, those which have the strongest mutual attractions will enter first into union: hence has arisen the above term. If I pour dilute nitric acid upon a mixture of lime and magnesia, the acid will dissolve the lime in preference to the magnesia.

* The *test-papers* used in the laboratory are generally *blue litmus* paper, for the detection of acids, and the same *reddened by a weak acid*, for the detection of alkalis; the acids render the former *red*, and the alkalis restore the *blue* of the latter. Paper tinged yellow by *turmeric* is also useful in the detection of alkalis, which change it to a more or less deep *reddish-brown*. Mr. Alfred Taylor re-

commends unsized paper, tinged by a strong infusion of the petals of the red rose, as a more delicate test for alkalis than turmeric: in a very strong alkali it is turned greenish-brown, but when the alkaline solution is very dilute, its reaction is extremely delicate, and it becomes bright green: it will thus indicate alkali where turmeric is not visibly discoloured.

The knowledge of this fact leads to the inference that lime would separate magnesia from its combination with nitric acid; and, accordingly, if lime-water be added to a solution of nitrate of magnesia, nitrate of lime is formed, and magnesia is thrown down or *precipitated*.

Upon this principle *tables of attraction* have been constructed, in which the substance, whose affinities are to be represented, is placed at the head of a column, and the bodies with which it combines beneath it, in the order of their respective attractions; thus the affinity of *sulphuric acid* for several bases would be shown as annexed.

SULPHURIC ACID.

Baryta.
Strontia.
Potassa.
Soda.
Lime.
Magnesia.
Ammonia.

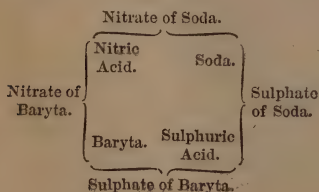
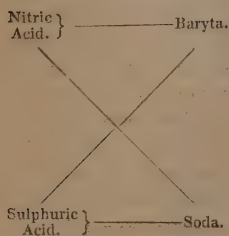
From this table it would appear that *baryta* separates sulphuric acid from its compounds with all the inferior substances, and that *ammonia* is separated by all that are above it; there are, however, many circumstances which interfere with the usefulness and accuracy of such tables; in some cases the volatility, and in others the insolubility of one or other products influence the results; and sometimes there are apparent anomalies in the mutual agencies of bodies, which subvert the order of arrangement. This is especially the case in the decomposition of certain insoluble compounds by soluble salts. One of these, originally noticed by M. Dulong, (*Ann. de Chim.*, LXXXII., NICHOLSON'S *Journ.*, 35 and 36,) has been pointed out by Mr. R. Phillips (*Journal of Science and the Arts*, vol. i., p. 80). He found that, on boiling carbonate of baryta in a solution of sulphate of potassa, sulphate of baryta and carbonate of potassa were formed; and he also found that, on reversing the experiment, by boiling sulphate of baryta in a solution of carbonate of potassa, carbonate of baryta and sulphate of potassa were produced. The inferences deducible from Dulong's researches upon this subject are, that all the insoluble salts are decomposed by the carbonates of potassa or soda; but that a mutual exchange of principles of these salts cannot in any case be complete: and that all the soluble salts, of which the acid forms with the base of the insoluble carbonate an insoluble salt, are decomposed by these carbonates until the decomposition has reached a certain limit, which it does not pass. (URE'S *Dict.*, Art. ATTRACTION.)

In the mutual decompositions of steam by iron, and of oxide of iron by hydrogen, we have another apparent anomalous case of chemical action. When steam is passed over red-hot iron, a portion of it is decomposed, hydrogen gas is evolved, and oxide of iron is formed; whence we should infer that the affinity of oxygen is greater for iron than for hydrogen. But if hydrogen gas be passed over red-hot oxide of iron, steam is formed and the iron reduced to the metallic state; here the affinity of oxygen appears greater for hydrogen than for iron. But in regard to this result it has been ingeniously remarked by Professor Graham (*Elem. of Chem.*, Part 2), "that it is obviously connected with the relative proportion between the hydrogen and the steam which are at once in contact with the metal and its oxide at a red heat. When steam is in excess, water is decomposed, but when hydrogen is in excess, oxide of iron is decomposed; and why? because the excess of steam in the first case is an atmosphere into which hydrogen can diffuse, and the disengagement of that gas is therefore procured; but in the second case the

atmosphere is principally hydrogen, and represses the evolution of more hydrogen but facilitates that of steam. The affinity of iron and hydrogen for oxygen, at the temperature of the experiments, is so nearly balanced that the one affinity prevails over the other, according as there is a proper atmosphere into which the gaseous product of its action may diffuse. This affords an intelligible instance of the influence of mass or quantity of material, in promoting a chemical change; the steam, or the hydrogen, as it preponderates, exerting a specific influence in the capacity of a gaseous atmosphere." The subject of the diffusion of gases referred to in this quotation will be explained in the chapter on *Hydrogen*.

In cases of *simple attraction*, or affinity, one body separates another from its combination with a third. Thus, when potassa is added to a solution of sulphate of zinc (composed of sulphuric acid and oxide of zinc), the oxide of zinc is separated, and sulphate of potassa is produced; or when sulphuric acid is dropped into a solution of nitrate of baryta, sulphate of baryta is precipitated.

In cases of *double decomposition*, two new compounds are produced; as when a solution of nitrate of baryta is mixed with a solution of sulphate of soda, the results are a precipitate of sulphate of baryta, and a solution of nitrate of soda.



These cases of double decomposition are sometimes conveniently illustrated by *diagrams*, which may either be constructed so as merely to show the result of the change, or, where required, they may also exhibit the composition of the acting bodies. In the case just alluded to, the substances before mixture are shown by parallel lines, and after mixture by diagonal lines.

Or a more complete view of the change is given in the annexed diagram, where the bodies, before mixture, are placed upon the outside of the perpendicular lines: their component parts are shown within them; and the new results on the outside of the horizontal lines.

§ 3.—CHEMICAL EQUIVALENTS AND THE ATOMIC THEORY.

A most important result of chemical attraction is, *that bodies combine in certain proportions only*. Thus, in the case just cited, of the combination of baryta with sulphuric acid, to form *sulphate of baryta*, it is found, that in that compound, whether formed by nature or art, by single or double decomposition, the sulphuric acid and baryta always bear a certain definite relation to each other, and are contained in it in the relative proportions, by weight, of 40 sulphuric acid and 77 baryta: that is, these relative weights exactly saturate or neutralize each other; if we suppose sulphate of baryta to be composed of *one atom* of sulphuric acid

and one atom of baryta, then the above numbers may be called the *atomic weights* of those substances, and an atom of sulphuric acid being = 40 and of baryta = 77, the atom of sulphate of baryta will be $(40 + 77) = 117$: these numerical proportions have been sometimes called *representative, or combining numbers*, or more commonly, for a reason which will presently be apparent, *equivalent numbers* or *proportionals*.

But, sulphuric acid and baryta are not elementary substances, they are both compounds, and are consequently termed the *proximate elements* of sulphate of baryta; sulphuric acid consists of sulphur and oxygen, and baryta consists of barium and oxygen; the *ultimate elements*, therefore, of sulphate of baryta, are sulphur, barium, and oxygen: hence also sulphuric acid and baryta are called *compound atoms*; but, in them, the same general law of definite proportionals holds good, for sulphuric acid consists of 16 sulphur and 24 oxygen, which, added together, produce the *compound equivalent* 40; and baryta consists of 69 barium and 8 oxygen, making 77, the *equivalent* of baryta or oxide of barium.

Another essential fact in reference to chemical combination is, that where one substance, A, combines in more than one proportion with another substance, B, the second, third, &c., proportions of B bear a very simple ratio to each other. Thus, mercury combines with oxygen in two proportions, forming the *black oxide* and the *red oxide* of mercury. In the former, 200 parts of mercury are combined with 8 of oxygen, and in the latter, 200 parts of mercury are combined with 16 of oxygen. Here it is obvious that the quantity of oxygen in the *first*, is to that in the *second* compound as 1 to 2. So that, assuming 200 to be the atomic weight of mercury, and 8 the atomic weight of oxygen, we should call the *black oxide* a compound of 1 atom of mercury and 1 atom of oxygen, and the *red oxide* a compound of 1 atom of mercury and 2 atoms of oxygen.

In other cases, the relative proportions of the components are to each other, as 1 to $1\frac{1}{2}$, 1 to $2\frac{1}{2}$, &c.; or, what amounts to the same thing, as 2 to 3, 2 to 5, &c. Thus, there are two oxides of iron; in the *black oxide*, 28 parts of iron are combined with 8 of oxygen, and in the *brown oxide*, with 12 of oxygen. Here, the quantity of oxygen in the *first* is to that in the *second* as 1 to 1.5. There are also two acids of arsenic; in the *arsenious acid*, 38 parts of arsenic are combined with 12 of oxygen, and in the *arsenic acid* with 20 of oxygen; numbers which are to each other as 1.5 to 2.5 or as 3 to 5. These cases, however, are by no means of such frequent occurrence as the former.

The simple ratio which the *weights* of the combining elements are thus seen to bear to each other, involves an equally simple law in respect to combining *volumes*, where substances either exist, or may be supposed to exist, in the state of gas or vapour. Thus, water may be considered as a compound of 1 atom of hydrogen and 1 atom of oxygen, the relative weights of which are to each other as 1 to 8; hence the equivalent of the atom of water will be $(1 \text{ hydrogen} + 8 \text{ oxygen}) = 9$. But oxygen and hydrogen exist in the gaseous state, and the weights of equal *volumes* of those gases (or in other words, their relative densities, or specific gravities), are to each other as 1 to 16; hence 1 *volume* of hydrogen is combined with $\frac{1}{2}$ 1 *volume* of oxygen, to form 1 *volume* of the vapour of water or steam: for the specific gravity of steam, compared with hydrogen, is as 9 to 1.

Hydrogen. 1	Oxygen. 8	=	Steam. 9
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The annexed diagrams, therefore, will represent the combining *weights* and *volumes* of the elements of water, and of its vapour.

To give another instance: hydrochloric acid gas is considered as a compound of 1 atom of hydrogen and 1 atom of chlorine, their respective *weights* being 1 and 36, and that of the resulting hydrochloric acid 37. Now, the specific gravity of hydrogen to chlorine is also as 1 to 36, and of hydrogen to hydrochloric acid as 1 to 18.5. Hence it is obvious, as in this

Hydrogen. 1	Chlorine. 36	=	Hydrochloric Acid. 37
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diagram, that 1 *volume* of hydrogen and 1 *volume* of chlorine combine to form 2 *volumes* of hydrochloric acid.

These instances, therefore, will suffice to show that there is the same simple relation in the *volumes* of the compounds as in their *weights*; 1 volume of hydrogen and 0.5 a volume of oxygen producing 1 volume of aqueous vapour; and 1 volume of hydrogen and 1 volume of chlorine producing 2 volumes of hydrochloric acid. In the latter case, and there are many similar instances, the equivalent, or atomic *weights*, correspond with the specific gravities in reference to hydrogen as = 1, the gases combining volume for volume, and producing a compound gas, the volume of which is equal to the united volumes of its constituents.

As a further illustration of the whole subject of definite proportionals, and of the atomic theory, in reference to weights and volumes, I subjoin a table of the compounds of *nitrogen* and *oxygen*: those elementary bodies unite with each other in no less than 5 proportions, and in the simplest ratios, forming two oxides and three acids.

	Atoms or equivalents of Nitrogen and Oxygen.		Weights of the atoms or equivalents of Nitrogen and Oxygen.		Atomic weight of the compound.	Volumes of Nitrogen and Oxygen.		Resulting volume of the compound.
	N.	O.	N.	O.		N.	O.	
1 atom of the protoxide of nitrogen consists of . . }	1	1	14	8	22	1	0.5	1
1 atom of the deutoxide . . }	1	2	14	16	30	1	1	2
1 atom of the hyponitrous acid }	1	3	14	24	38	1	1.5	
1 atom of the nitrous acid . . }	1	4	14	32	46	1	2	1
1 atom of the nitric acid . . }	1	5	14	40	54	1	2.5	

86 Nitrate of Soda.			
Nitric Acid 54	+	Soda 32	
131 Nitrate of Baryta.		72 Sulphate of Soda.	
Baryta 77	+	Sulphuric Acid 40	
Sulphate of Baryta. 117			

It has been above stated that 40 parts of sulphuric acid (or 1 atom) are neutralized by 77 (or 1 atom) of *baryta*. Now we find that 40 parts of sulphuric acid are neutralized by 32 of *soda*; hence, 32 will be the atomic weight, or equivalent of *soda*: if we now refer to nitric acid we shall find that 77 parts of *baryta* neutralize 54 of nitric acid, and that 32 of

soda neutralize the same quantity of that acid. Supposing, therefore, we decompose *nitrate of baryta* by *sulphate of soda*, it follows that the newly-formed salts will still be *neutral*, as in the preceding diagram, to which the *equivalent* numbers of the acting substances are annexed; from which it appears that 131 parts of *nitrate of baryta*, consisting of 77 baryta and 54 nitric acid, are required to decompose 72 parts of *sulphate of soda*, composed of 32 soda and 40 sulphuric acid; and that the results of this decomposition are 86 parts of *nitrate of soda*, composed of 54 nitric acid and 32 soda, and 117 *sulphate of baryta*, composed of 40 sulphuric acid and 77 baryta.

If we, therefore, are acquainted with the *equivalent numbers* of the respective *bases* and *acids*, we at once know the relative quantities required for *saturation*, and consequently the composition of all the *neutral salts*, as will be evident from inspecting the following table:—

ACID.	EQUIVALENT.	BASE.	EQUIVALENT.
Iodic	165	Baryta	77
Bromic	118	Strontia	52
Chloric	76	Potassa	48
Selenic	64	Soda	32
Nitric	54	Lime	28
Sulphuric	40	Magnesia	20
Oxalic	36	Lithia	18
Carbonic	22	Ammonia	17

Here we find, for instance, that 40 parts of sulphuric acid saturate 48 of potassa to form 88 of *sulphate of potassa*, for the decomposition of which would be required 131 of *nitrate of baryta*, containing 54 of nitric acid and 77 of baryta. We may also remark the different quantities of the different bases that are required to saturate a given weight of any of the acids, and *vice versâ*: thus, 77 of baryta, and only 17 of ammonia are required to saturate 54 of nitric acid; and 28 of lime, which are saturated by 22 of carbonic acid, require 165 of iodic acid for the same purpose.

These tables are of great value to those who conduct chemical operations upon the large scale, in the processes of arts and manufactures, guiding them in the quantity of materials which they require, and pointing out the proportions of the products which should be obtained; and when applied, as suggested by Dr. Wollaston in his account of "A Synoptic Scale of Chemical Equivalents," (*Phil. Trans.*, 1814,) to a *sliding-rule*, divided upon the principle of *Gunter's scale*, they furnish the practical as well as the theoretical chemist with an admirable instrument of reference, for the purpose of facilitating and verifying his experimental and calculated results. The form of this instrument, which I recommend to the student*, is a box-wood scale, about two feet two inches long, consisting of a moveable slider with a logometric line of numbers upon it, and a corresponding series of numbers upon the rule itself; upon the *rule* the simple substances are also arranged, each opposite to its respective equivalent: the equivalents of the compounds may, by those who have competent experience, be easily deduced from those of the elements; but, for the convenience of others, and to avoid perplexing the scale with a multiplicity of terms, a separate table accompanies it, containing a

* They are made by Newman, No. 122, Regent Street, and Palmer, 60, Newgate Street.

copious list of compound equivalents. One of the commonest uses of this scale is to ascertain the relative proportions of the elements, in variable quantities of their compounds; for instance, I know that the equivalent of *chlorine* is 36, and of *sodium* 24, and consequently that the equivalent of *chloride of sodium* (or common salt) is $(36 + 24) = 60$. But I wish to ascertain how much of each of the elements is contained in 95 of salt; I therefore bring the number 95 upon the slider opposite to 60 upon the scale, and I now find the number 57 opposite to 36, and the number 38 opposite to 24; hence 95 parts of *chloride of sodium* consist of 57 of *chlorine*, and 38 *sodium*. These and the other uses of this scale are soon learned by a little practice, or by reference to Dr. Wollaston's paper, above quoted, or to Mr. FARADAY'S *Manipulation*.

The doctrine of equivalents furnishes the analytical chemist, in the first place, with a valuable test of the accuracy of his experimental results, which of course, if correct, will not deviate from the above laws; it also enables him, in many instances, to infer the composition of a substance, where direct experiment is unattainable, and this in more ways than one. It was long, for instance, before *magnesium* (the metallic base of magnesia) was obtained, but analogy led chemists to conclude that magnesia was a *protoxide* of a metal, that is, a compound of 1 atom of metallic base, with 1 atom of oxygen. The composition of magnesia, therefore, was inferred from the composition of its *sulphate*, consisting of 1 atom of sulphuric acid = 40 united to 20 of magnesia; now 20, which thus presents itself as the atomic weight of magnesia, must include an atom of oxygen = 8; and 8 deducted from 20, leaves 12 as the inferred weight of the atom of *magnesium*. In the same way the composition of lime was inferred to be 20 calcium and 8 oxygen, for it was found that sulphate of lime consisted of 40 sulphuric acid and 28 lime, and as the oxygen in the *base* of a neutral *sulphate* is to that in the *acid* as 1 to 3, it became obvious that *lime*, or *protoxide of calcium*, must be constituted as above stated.

To give another instance of a similar application of the atomic theory: it was found that chlorine expelled oxygen from lime, and it was ascertained that for every 28 parts of lime so decomposed, 8 parts of oxygen were evolved, and 56 parts of chloride of calcium formed; now deducting 36 (the equivalent of chlorine) from 56, 20 remains, as the equivalent of calcium.

More complicated instances of such extensions of this theory will be given afterwards, especially among its applications to *organic products*; my object in the preceding paragraphs has been to divest it of all hypothetical difficulty, and to present it to the student as involving a series of important practical applications, and as founded upon the basis of experiment. Those who would view it in reference to ancient atomic doctrines, and to the more obscure parts of molecular philosophy, may consult Dr. DAUBENY'S *Essay on the Atomic Theory*, and Dr. PROUT'S *Bridgewater Treatise*.

I shall now merely add a few words in further explanation of the *mode of determining atomic weights, or equivalent numbers*. They are founded upon careful analyses of the simplest combinations of the most important elements: among these we may, as an instance, select *water*; the most

rigid analytical researches concur in representing this fluid as constituted, *per cent.*, of 11.1 hydrogen, and 88.9 oxygen. Now, if we determine upon hydrogen as *unity*, or = 1, then $11.1 : 88.9 :: 1 : 8.009$; or, the hydrogen is to the oxygen very nearly in the ratio of 1 to 8; and assuming water to consist of 1 *atom* of hydrogen united to 1 *atom* of oxygen, the atomic weight of the former being = 1, that of the latter would be = 8. In *hydrochloric acid*, which, as already stated, is a compound of hydrogen and chlorine, these elements bear to each other the relation of 1 to 36; hence 36 is assumed as the *atomic weight*, or *prime equivalent* of chlorine. If I now wish to determine the equivalent of a *metal*, I select its *protoxide*, and ascertain what *weight* of the metal is combined in such oxide, with 8 parts of oxygen: thus in regard to *soda*, I find it constituted *per cent.* of 25 oxygen and 75 sodium; and $25 : 75 :: 8 : 24$; hence the number 24 is assumed as the *equivalent of sodium*. In the same way I may resort to the analysis of *chloride of sodium*, 100 parts of which consist of 60 chlorine and 40 sodium; and $60 : 40 :: 36 : 24$; thus the former result is verified by the analysis of a second compound.

The advantages of assuming *hydrogen* as = 1 or *unity*, and thence deducing the other equivalents, are such as to have led to its very general adoption in this country; as it is the substance which combines in the smallest relative weight, all other substances may be represented by numbers which are *multiples* of its equivalent, and may, for all ordinary purposes of demonstration and research, be *whole numbers*; but to this subject I shall again recur. Some represent hydrogen by 10, and some by 100; in these cases oxygen is of course 80 or 800, and chlorine 360 or 3600, &c. Others adopt *oxygen* as *unity*, in which case hydrogen becomes one-eighth of that unit, and is represented by 0.125, chlorine by 4.5, sodium by 3, &c.; but this system is extremely inconvenient, in consequence of the perpetual and necessary recurrence of fractions, especially as concerns the retention of equivalents by the memory. The equivalents used by Berzelius have reference to oxygen as 100.*

The practical uses and applications of the atomic theory, and further illustrations of the researches upon which it is founded, will occur in almost every succeeding page of this book. It has been justly observed by Sir John Herschel, that the extreme simplicity which characterizes this theory, is itself no unequivocal indication of its elevated rank in the scale of physical truths. (*Prel. Disc.*, p. 305.)

* The extreme confusion resulting from the adoption of a series of equivalent numbers founded upon the assumption that water is a compound of 2 atoms of hydrogen and 1 atom of oxygen, and the incongruities and contradictions which such a hypothesis involves, must be too evident to all who read the works of the eminent authors who speak in that language.

CHAPTER IV.

ELECTRICITY.

MANY of the phenomena of electricity are so remarkable, and so easily exhibited, as long to have attracted general attention: by the natural philosopher they have been studied with much precision and success; and, more lately the discovery of the relation of the *electrical* to the *chemical* powers of matter, and to *magnetism*, has opened an entirely new field of research.

We are ignorant of the *nature* or *cause* of electrical phenomena, but for the convenience of description and discussion it has been customary to refer them to the presence of a highly attenuated and subtile form of matter, which has been termed the *electric fluid*. The existence, however, of such a fluid, or of any peculiar form of matter as productive of electrical phenomena, is entirely hypothetical, and merely assumed to facilitate our reasoning upon the subject.

Inasmuch as electrified bodies are found to present themselves in *two opposite or distinct states*, it has been presumed that the electric fluid exists in all forms of matter; that, under ordinary circumstances, it is in a *state of equilibrium or quiescence*; and that, when this state is so disturbed as to occasion either its *redundance* or *deficiency*, the bodies then become *electrically excited*: upon this view of the cause of electricity, which originated with Franklin, the opposite states have been termed *positive* and *negative*. Others ascribe the phenomena to the presence of *two electric fluids*, supposed to reside in *glass* and *resin*, and hence distinguished by the terms *vitreous* and *resinous*. This hypothesis, which originated with Du Fay, has, under some modifications, also been very generally adopted; it has been assumed that the two electric fluids are universally diffused; that they are infinitely subtile and elastic, and each *repulsive of its own particles, but attractive of those of the opposite kind*; these forces being equal at equal distances, and varying inversely with the square of the distance*. In the ordinary or quiescent state, these fluids are supposed to be *combined* with, and exactly to *neutralize*, each other; and electric excitation is attributed to their *separation*, or to the *decomposition* of the neutral fluid. The first of these hypotheses is recommended by its simplicity, and by the facility with which it enables us to reason upon the greater number of electrical phenomena; but there are cases in which the second appears most consistent; so long, however, as the definitions which we shall afterwards give, of the terms *positive* and *negative*, are distinctly understood, the adoption of either hypothesis is matter of little importance, always bearing in mind that both states, or fluids, are common to all matter, and that they are always coexistent.

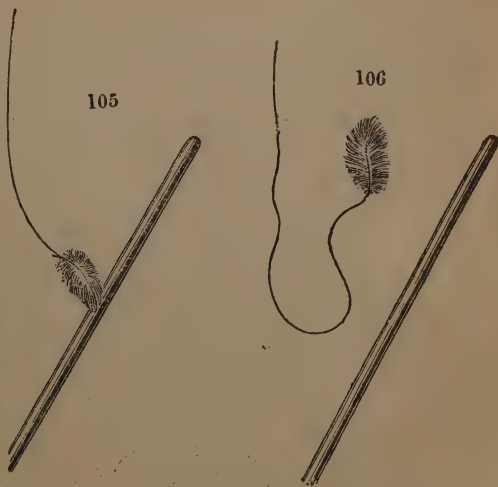
* Coulomb supposed the two electric fluids to be possessed of equivalent properties, neutralizing each other's elasticity, like oxygen and hydrogen combined.

§ 1.—ELECTRICAL EXCITATION.—ATTRACTION AND REPULSION.

THE simplest indication of electricity is that which is observed when certain resinous and vitreous bodies are subjected, in a dry and warm state, to gentle friction; as when a piece of sealing-wax is rubbed with flannel, or a glass rod with a piece of silk; in these cases the sealing-wax and the glass acquire the property of attracting and repelling light substances; and they are said to be *electrically excited*. Such properties seem first to have been observed in, and supposed peculiar to, *amber*; and hence the term *electricity*, from the Greek word *ηλεκτρον*, signifying *amber*. Independent of these attractive and repulsive powers, there are other equally curious properties observed in the electrically-excited bodies; in the dark they appear *luminous*, shining, whilst rubbed, with flashes of a blueish light; and, if held near the face, they produce a singular tickling sensation. We find, moreover, that this electrical excitation is transient; that it gradually disappears, and that if the hand be passed two or three times over the surface of the sealing-wax, or of the glass, all signs of electricity are lost. A very light downy feather, perfectly clean and dry, and suspended in any convenient way by a long thread of *white* sewing silk, so as to be as independent as possible of surrounding bodies, is a most delicate and useful indicator of this form of electrical excitation, and may be used in the following experiments.

1. Provide a glass tube, about three feet long, and three-fourths of an inch diameter, and having wiped it perfectly clean and dry, rub it gently with a warm silk handkerchief; it will become electrically excited; and, on approaching the feather, will immediately *attract* it; but, on gently withdrawing, and again bringing it near to the feather, the feather will be steadily *repelled*; so that it will be impossible, for a short time, to get it to touch the tube: after a while, however, it again flies to, or is attracted by, the tube, and then again repelled as before. The annexed cuts (figs. 105, 106,) represent the appearance of the feather when attracted and when repelled.

This apparently trifling experiment teaches us the following important elementary fact: it shows that the feather, having received electricity from the glass by direct contact, is repelled by it; and, consequently, that *bodies similarly electrified repel each other*; for we assume the feather to have *received* a portion of the electricity of the glass, and we know that the repulsion is *mutual*.



2. Rub a large stick of red sealing-wax with a thick roll of dry and warm flannel; the sealing-wax will thus be rendered electrical, and will act upon the feather *apparently* in the same way as the glass; that is, first attracting and then repelling it; and the moment that the feather has received the electricity of the wax, those bodies also become mutually repulsive.

3. Warm a sheet of foolscap paper, folded in the usual way, before the fire, and rub it gently upon a clean polished table with a large piece of Indian rubber; then suddenly open the sheet, and hold its interior towards the feather, which will be attracted and repelled, as in the preceding cases of glass and wax.

There are a number of other substances which become electrical by friction, such as white and black silk drawn gently over each other, as is commonly observed with silk stockings; the back of a clean cat gently rubbed with the dry and warm hand; long, clean, and dry hair, combed in frosty weather; silk tassels and fringes, and so on: but the instances above cited are sufficient, and we may now proceed to a second set of experiments with the same apparatus.

1. Excite the glass tube as before, and electrize the feather, so as to render it *repulsive* of the tube; then bring the excited sealing-wax near the feather, and it will not be repelled as by the glass, but will be immediately *attracted*, by it.

2. Reverse the experiment, and having electrized the feather by sealing-wax, bring the excited glass rod near it, when, instead of being further *repelled* it will be *attracted*.

3. If the feather be suspended between the excited wax and the excited glass, it will vibrate to and fro, being *alternately attracted and repelled*.

These experiments show that there is a *difference in the electricities of the glass and sealing-wax*, and that bodies rendered *repulsive* by glass are *attracted* by wax; and *vice versâ*. We had previously found that bodies similarly electrified repel each other; we now observe that *bodies dissimilarly electrified attract each other*.

These dissimilar electricities, in reference especially to the above methods of producing them, were originally termed *vitreous* and *resinous*; for these, the terms *positive* and *negative* are now more commonly substituted; and the two states may be represented by the symbols *plus*, + and *minus* -. The feather electrized by *glass* is said to be in a *positive* state, and that by *sealing-wax*, *negative*.

Still retaining the simple apparatus that we set out with, we may now proceed as follows:—1. Fold the silk in such a way as to keep the hand as far as possible from the glass tube; then rub the tube with it, and electrize the feather, which will now be *repelled*; whilst it retains this repulsive state, in regard to the tube, approach it with the part of the silk which had rubbed the glass, and it will be found to be *attracted*. From this experiment we should conclude that the *silk* and the *glass* were in *opposite* electric states: we have already called the glass *positive*; the silk, therefore, must be *negative*. The experiment may be varied as follows:—

2. Hold the handkerchief as before, and having warmed it, rub it

with the tube; then bring it near the feather, which it will first attract and then repel: whilst the feather is thus *repelled* by the silk, approach it with the excited glass, by which it will be immediately *attracted*. It is obvious, therefore, that the glass and the silk are in *opposite* states.

3. If we roll up the flannel so as to keep the rubbed part at a distance from the hand, then rub it with the sealing-wax, and bring it to the feather, the latter will be immediately attracted by the flannel, and then repelled: if we now approach it with the excited wax, instead of being more powerfully *repelled*, it will be instantly *attracted*. Hence, having agreed to call the electricity of the wax *negative*, that of the flannel must of course be *positive*; for it is evidently of the opposite or dissimilar kind.

Here, then, we have developed another important electrical law, showing that *one kind of electricity cannot be produced without the other*; that when a body is *positive*, some part of the exciting arrangement is *negative*. In the above case of glass and silk, the former is positive, and the latter negative: and in the case of sealing-wax rubbed by flannel, the wax is negative, and the rubber acquires a positive state.

4. That this is so, may be further shown as follows:—render the feather positive by the contact of the excited glass; then approach it with the excited flannel, and it will be found to be repulsive of the flannel; that is, to possess a *similar* electrical state.

5. Electrize the feather with the excited wax, which will render it *negative*, and then approach it with the excited silk; the silk will continue to repel the feather, and hence is similarly electrized, or *negative*.

Delicate instruments show us, that in almost all cases of *friction*, under the precautions above described, bodies become electrically excited: and that the same body may become either positive or negative, according to the circumstances under which it is excited. Smooth glass, for instance, becomes positive when rubbed with a piece of woollen cloth, but rough glass rubbed in the same way becomes negative; and sealing-wax, which becomes negative when rubbed by flannel, becomes positive when rubbed against tin-foil or mercury. A cat's back is said always to exhibit positive electricity; but it is probable that no peculiar kind of electricity is inherent in any one body; it will even vary with the mechanical state of the surface and the mode of friction; so, polished glass becomes positive when rubbed upon silk, but rough glass becomes negative; both become negative against a cat's back; and when similar substances are rubbed together, that, the friction of which is limited to the least extent of surface, is usually negative: thus, when two similar silk ribands are excited by drawing the one lengthways over the other, that which has suffered friction on its own length becomes positive, and the other negative. The following table, chiefly from the experiments of Cavallo, further illustrates these effects.—(SINGER'S *Elements of Electricity*, p. 33.)

	Becomes	by friction with
The back of a cat . . .	Positive . . .	Every substance tried.
Smooth glass . . .	Positive . . .	Everything except cat-skin.
Rough glass . . .	Positive . . .	Dry oiled silk, sulphur, metals.
	Negative . . .	Wools, quills, wood, paper, sealing-wax, white-wax, common silk; the hand.
Tourmaline . . .	Positive . . .	Amber; air from bellows.
	Negative . . .	Diamonds; the hand.

	<i>Becomes</i>	<i>by friction with</i>
Hare's-skin . . .	Positive . . .	Metals, silk, leather, hand, paper, baked wood.
	Negative . . .	Other finer furs.
White silk . . .	Positive . . .	Black silk, metals, black cloth.
	Negative . . .	Paper, hand, hair, weasel's skin.
Black silk . . .	Positive . . .	Sealing-wax.
	Negative . . .	Hare, weasel, and ferret fur; brass, silver, iron, hand, white silk.
Sealing-wax . . .	Positive . . .	Some metals.
	Negative . . .	Hare, weasel, and ferret fur, hand, leather, woollen cloth, paper, some metals.
Baked wood . . .	Positive . . .	Silk.
	Negative . . .	Flannel.

In regard to the above table, Mr. Singer observes that iron, lead, and bismuth, render sealing-wax negative, the other metals positive; but the least difference in the condition of the materials occasions varieties in the result: with the same rubber (an iron chain) positive electricity may be excited in one stick of wax, and negative in another, if the former be scratched and the latter smooth. *Æpinus* also found that two pieces of plate-glass, when rubbed on each other, were electrical when separated; but that although one was always positive and the other negative, the same plate sometimes exhibited the one, and sometimes the other electricity.

In the following list, the substances become positive with those which follow, but negative with those which precede each other; viz., oxalate of lime, fur, smooth glass, woollen cloth, feathers, paper, silk, gum-lac, rough glass.

§ 2.—ELECTRICAL CONDUCTORS AND NON-CONDUCTORS.

THERE are some substances which, when examined by the above-described methods, are not observed to become electrical. If we, for instance, rub a cylinder of *metal* with flannel or silk, it is perfectly inert when brought near the feather: but the exception here is apparent only; the substances previously used, such as glass and sealing-wax, are *non-conductors* of electricity; that is, they receive and retain it upon the excited surface only; but a bar of metal is a *conductor*, and when electricity is produced upon it by friction, it immediately spreads over its whole surface, and is carried off, as it were, by the hand, to the earth and all surrounding conductors. To show that the metal actually is excited in the same way as glass, attach it to some non-conductor: for instance, attach a cylinder or plate of brass to a stick of sealing-wax, which may serve as its handle; then rub the brass against a dry and warm flannel, and, taking care not to touch any part of it with the hand, bring it near the feather, which will be attracted, and then repelled, precisely as by the glass and wax. In these cases the metals usually acquire negative electricity.

We now, then, can understand the division of bodies into *conductors* and *non-conductors*. There are also a set of bodies intermediate between the above extremes, which are called *imperfect conductors*. The non-

conductors, readily exhibiting their electricity by friction, are often called *electrics*, in opposition to the metals and other good conductors, which are called *non-electrics*. The electrics, from their power of preventing the passage or transfer and escape of electricity, are also sometimes termed *insulators*. Thus, a brass rod mounted upon a stem or foot of glass, or sealing-wax, or a wire suspended by silk thread, is said to be an *insulated conductor*.

The metals are by far the most perfect conductors; next to them come well-burned charcoal and plumbago; then some of the concentrated acids, and strong saline solutions. Water, rarefied air, most vapours, and many stony bodies and metallic ores, are imperfect conductors. Shell-lac is the most perfect non-conductor, and an excellent substance to use wherever good insulation is required*. Sulphur and wax are also non-conductors; and so is glass, which, though in this respect much inferior to some other substances, is from the convenience of its application, the usual insulator employed in all common electrical apparatus. Raw and bleached silk stands high upon the list of non-conducting substances; but dyed silk is often a partial conductor, in consequence of the substances used to colour it: hence, in the above experiments, we have advised *white* silk for the suspension and insulation of the feather. It is also stated by Henley, that black hair conducts better than white (*Phil. Trans.* 1776), as illustrated in the case of a bullock struck by lightning. Dry air, and baked wood, are non-conductors. There is a gradual transition in bodies from what are termed perfect conductors, to perfect non-conductors; the following list exhibits the principal of these:—

CONDUCTORS.	IMPERFECT CONDUCTORS.	NON-CONDUCTORS.
Metals	Water	Spermaceti
Charcoal	Damp wood	Glass
Plumbago	Alcohol	Sulphur
Fused chlorides	Damp air	Fixed oils
—— iodides	Some oils	Resins
—— salts	Vegetable and	Ice
Strong acids	animal bodies	Diamond
—— alkaline solutions.	generally.	Shell-lac
		Oxalate of lime
		Dry gases and air.

There is no constant relation between the *states* of bodies and their conducting powers. Among *solids*, for instance, metals are conductors; resins non-conductors: among *liquids*, strong alkaline and acid solutions are good conductors; water is an imperfect conductor; many oils are non-conductors. Potassa, protoxide of lead, chloride of sodium, iodide of zinc, many salts, and other bodies, are non-conductors in their solid state, but conduct when liquified by heat. Sulphur, phosphorus, resins, iodide of sulphur, and several other solid bodies, do not, on the contrary, acquire conducting power on assuming the liquid state. (FARADAY, § 394,

* According to Erman, (*Gilb. Ann.*, xi., 143), a thread of gum-lac insulates ten times as well as silk. A needle of sealing-wax remains for some days excited. A capillary bore lessens the insulating power of glass. The dissipation

of electricity by the atmosphere is nearly in the triplicate ratio of its moisture. It is also stated, that an electric jar is discharged if put into a vibratory state, as by sounding it like a harmonica.

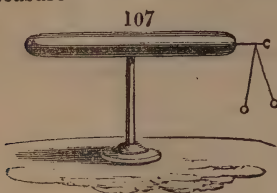
&c.) Glass, when cold, is a non-conductor; but when red-hot, it is a conductor: the diamond is a non-conductor: but pure and well-burned charcoal, which is merely another form of diamond, is among the best non-metallic conductors*.

We may form some idea of the retardation which electricity suffers in passing through imperfect conductors, from the statement of Mr. Cavendish (*Phil. Trans.*, 1776), according to whom, iron-wire conducts 400 million times better than pure water; sea-water, (with one-thirtieth of salt) 100 times better; and a saturated solution of salt, 700 times better.

The enormous rapidity of the progress, or supposed progress of the electric fluid through long trains of conductors, was first experimented upon by Watson (*Phil. Trans.*, 1748): he could observe no perceptible time occupied in its passage through a circuit of 12,276 feet. This curious subject has lately been investigated by Mr. Wheatstone (*Phil. Trans.*, 1834, p. 583), according to whom, electricity moves through a copper wire, with the velocity of 400 feet in the ten-thousandth part of a second; or, through 4 million feet in a second. To this subject we shall afterwards recur in referring to the conducting powers of the metals, in regard to voltaic electricity.

§ 3.—ELECTROSCOPES AND ELECTROMETERS.

Electroscopes and *electrometers* are instruments by which changes in the electrical states of bodies are rendered evident, and their intensities measured.



One of the simplest of these (fig. 107) consists of two small pith-balls, suspended by very fine thread or silver-wire to the end of a small insulated conductor. When this receives electricity, the balls diverge, and the nature of the electricity by which they are diverged may be judged of, by approaching the conductor with a piece of excited

sealing-wax: if the divergence *increases*, it is the same as that of the wax or *negative*; if it *diminishes*, it is opposite to that of the wax, or *positive*.

Where a more delicate test of the presence of electricity is required,



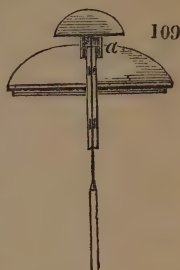
we substitute for the pith-balls two small slips of gold-leaf; and as these are apt to be deranged by the slightest motion of the air, it is necessary to enclose them in a glass cylinder, sufficiently capacious to allow of their divergence. They are connected with the brass cap of the instrument, which is used in the same way as the preceding. This is commonly called *Bennet's gold-leaf electrometer*.

The delicacy of the gold-leaf electrometer is much increased by an improvement in the insulation of the leaves, which we owe to the late Mr. Singer.

It will appear hereafter that all substances may conduct electricity, and that the terms conduction and non-conduction therefore are so far incorrect: in employing them as above we refer

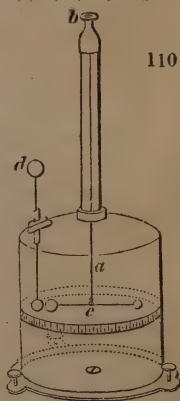
to their common acceptance. See, in reference to this subject, FARADAY'S *Experimental Researches*, § 1320 and 1326.

The instrument is constructed, as usual, with a glass cylinder surmounted by a brass cap, but the insulation is made to depend upon a glass tube, about four inches long, and one-fourth of an inch internal diameter, covered both on the inside and outside with sealing-wax, and having a brass wire of a sixteenth or twelfth of an inch thick, and five inches long, passing through its axis, so as to be perfectly free from contact with any part of the tube, in the middle of which it is fixed by a plug of silk, which keeps it concentric with the internal diameter of the tube. *a* is a brass cap screwed upon the upper part of this wire; it serves to limit the atmosphere from free contact with the outside of the tube, and also defends its inside from dust; to the lower part of the wire the gold-leaves are attached, and the whole mounted as usual, as represented, in section, by fig. 109. When a gold-leaf electrometer is to be employed in atmospherical investigations, the contrivance described by Mr. Ronalds (*Quart. Journ.* ii. 249) may be conveniently applied to it.



The *kind of electricity* by which the gold leaves are diverged may be judged of, as before, by approaching the cap of the instrument with a stick of excited sealing-wax: if it be *negative*, the divergence will increase; if *positive*, the leaves will collapse; upon the principle of the mutual annihilation of the opposite electricities; or that bodies similarly electrified repel each other, but that when dissimilarly electrified they become mutually attractive.

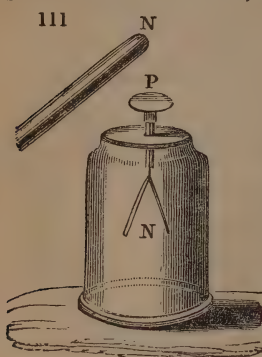
To ascertain the actual repulsive and attractive powers appertaining to weakly-electrified bodies, Coulomb ingeniously availed himself of the principle of torsion, and thus constructed his *electrical balance*. It consists of a fine metallic wire, *a*, fig. 110, one end of which is attached to the screw *b*, and to the other is suspended the horizontal needle *c*, composed of gum-lac or other non-conductor, and armed at one extremity with a gilt pith-ball, counterpoised at the other end by an index. The conductor *d* is a small wire with a ball at each end, passing through the glass receiver in which the needle is suspended, and having its lower ball opposed to that of the needle. By the screw *b*, the two balls are brought into contact, and the index then points to *o*, on the divided scale of degrees. On communicating a very feeble electrical power to the conductor, it transfers it to the moveable pith-ball, and *repels* it a certain number of degrees, proportional to the intensity of the acquired electricity, and measured by the power of torsion which it exerts upon the fine wire. By experiments made with this electrometer, it would appear that the electrical powers follow the law of gravitation, in being *in the inverse ratio of the squares of the distances of the acting bodies*. In the most delicate construction of the instrument, a single silk-worm's thread or a filament of spun glass is used instead of the wire.



By means of the gold-leaf electrometer, constructed as above, we dis-

cover the existence of very slight states of electrical excitation, which elude all common methods of detection. If the cap of the instrument be gently struck with a silk handkerchief, a powerful divergence may be given to the leaves, resulting from the friction of the metal and silk; if blown upon by a pair of bellows, electrical excitation is also indicated, depending probably upon the friction of the air upon the metal; and it will be found in the sequel, that we conveniently avail ourselves of this instrument to detect the evolution of electricity in a variety of other cases.

To determine the kind of electricity by which the leaves are repelled, we approach them, as before directed, either with an excited stick of sealing-wax, or a glass rod; if the divergence is increased by the former, it is *negative*; if diminished, *positive*; if increased by the glass, it is *positive*; if diminished, *negative*. In consequence of the law of excita-



tion by induction, it is sometimes supposed that this method of merely *approximating* the instrument, instead of actually touching it by the excited wax or glass, might lead to erroneous conclusions; but if we examine a little more particularly into the state of things, we shall find that, consistently with that law, *electro polarity* will be produced, and that consequently, the *gold leaves* will acquire the *same* electricity as that of the wax or glass, although the surface of the brass plate or cap of the instrument, immediately opposed to the wax or glass, may be in an opposite state.

Thus, let N (fig. 111) represent a piece of excited wax, *negative*; P the cap of the electrometer, *positive*; N the gold leaves, *negative*, that is, *similarly* electrified to the wax.

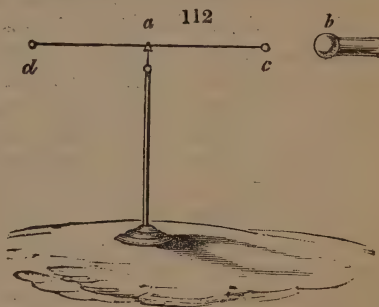
§ 4.—INDUCED ELECTRICITY.

WE have laid it down as a general rule, that no electrical *attractions* exist, except between bodies in *opposite* or *dissimilar* electrical states; and have shown that when any electrified body, such, for instance, as an excited stick of sealing-wax, is brought near other non-electrified bodies, they have a tendency to mutual attraction. This tendency exists among all surrounding substances; but such, of course, only, as have freedom of motion, are observed to move towards the excited electric: such as the suspended feather, particles of dust, and any other light and moveable bodies. Now, as these are *attracted* by the electrified body, it follows that they must previously be thrown into an *opposite* electric state, by the mere *proximity* of the excited electric; and this is really the case: whenever an electrified body is brought near to another in an un-electrified state, the surface of the latter, opposed to the former, becomes *oppositely* electrical, and is consequently *attracted* by it.

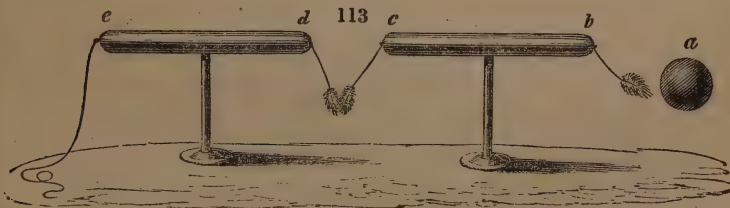
Electricity is thus said to be *induced* in the surrounding bodies by the vicinity of any excited electric: thus, when a highly-electric cloud hovers over the earth, that portion of the earth's surface opposed to the

cloud, becomes in an oppositely electrical state, and consequently attractive of the cloud; thus, during a thunder-storm, we often see an electric cloud perch upon the summit of a hill, and remain there till it has discharged its electricity, when it is wafted quietly away.

Electricity by induction presents many curious phenomena, which may here be stated generally, and more particularly explained afterwards. We have already said, that when an electrified body approaches another which is in its ordinary state, the surface of the latter opposed to the electrified body acquires an opposite state: this opposite electrical state, however, only belongs to the opposed surface; for the other side of the body, though also electric, is *dissimilarly* so. This statement may be rendered more intelligible by the following diagram:—Let *a*, fig. 112, represent a brass needle freely moving upon its centre, which is supported upon a glass foot. *b*, a conductor, *positively* electrified, and within a few inches of the pith-ball *c* attached to one of the points of the needle. We shall now observe that *c* is *attracted* by *b*, and may therefore infer that it is *negative*; and that this is really the case may be shown by



bringing near to the ball *c*, a stick of excited sealing-wax, by which it will be *repelled*. But if we now bring the sealing-wax towards the ball *d*, it will be *attracted* by it: here, then, by the *proximity* of the conductor *b*, we have induced in the needle *a* an *electro-polar* state; *b* being positive, *c* is negative, *d* positive. To explain this further by the help of our hypothesis: let us suppose the natural or quiescent electricity of *a* to be disturbed by the presence of *b*, which causes a portion of it to be repelled or driven from *c* to *d*. The end *c*, therefore, is *negative*, or *minus*, that is, it has *less* than its natural portion of electricity; and *d* is *positive*, or *plus*, because in it electricity is *accumulated*: in the centre *a* there will be a neutral point, in which no electricity is manifest. The state of the needle therefore is such, that negative electricity is accumulated at *c* and positive at *d*, and that they each gradually decrease towards the centre *a*. On the removal of the disturbing body *b*, the needle reverts to its ordinary state; or, in other words, the electrical equilibrium is restored.



The *polar arrangement* thus caused by induced electricity, may be carried to any extent: thus, suppose *a* in the preceding diagram, fig. 113,

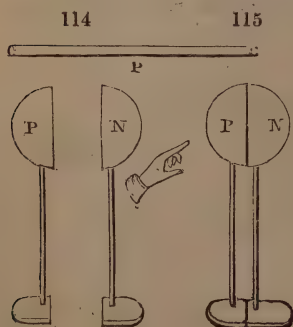
to represent a body *negatively* electrified, *b* would become positive, *c* negative, *d* positive, *e* negative, and so on, through any extent of conductors, the last being in communication with the earth. Thus the feather attached to the insulated conductor at *b*, is attracted towards *a*, and the feather *c* attracted by *d*; these feathers and surfaces being respectively in *oppositely electrical states*.

These illustrations will suffice to explain the meaning of the term *induction*, or induced electricity, without a knowledge of which many of the electric phenomena we are about to advert to, would be unintelligible: we shall afterwards find that it presents some very extraordinary consequences in reference to the distribution and accumulation of electricity, and the disturbance of the electrical equilibrium.

The actual electro-polar state of a conductor under induction is well shown as follows: place two gold-leaf electrometers about 18 inches apart, and connect their caps by an insulated wire lying across them; then approach *one* of them with an excited glass tube, which will cause both to diverge; whilst they are in this diverged state, lift off the intermediate wire, and then remove the inducing tube, and each electrometer will retain its divergence: on examining that which was nearest to the excited glass tube it will be found *negative*, and that which was at the other extremity of the wire will be *positive*; if we now, by means of a wire, with an insulated handle, reconnect the two caps, both electrometers will collapse, and lose all signs of electricity, showing that the negative and positive states were co-equal: a piece of wire with a handle of gum-lac is a convenient connector for the electrometers.

When in these experiments, the conductor electrified by induction is insulated (as it must be to exhibit its polar state), the accumulation of either electricity is of course feeble, being limited to the decomposition of the quantity of neutral electricity contained in it; but if one end of the conductor be connected with the ground, the supply is comparatively unlimited: this may be well shown by presenting the knuckle or a brass ball held in the hand to the prime conductor of the electrical machine; the opposed surface becomes oppositely electrical by induction, and a succession of sparks pass; but if the person be insulated, the induction is limited, as in the insulated conductor, and only two or three sparks are observed to pass.

The following experiments on induction I have taken from Mr.



Faraday's *Lectures*, and they are excellently adapted to class illustration. Provide two hollow brass hemispheres, or wooden ones covered with tin-foil, each mounted upon a lacquered glass stem standing upon a wooden foot (fig. 114), so that when placed together they may form the insulated sphere (fig. 115). Having thus placed them, approach them with an excited glass rod, and then remove it. On examining them by a gold-leaf electrometer, they will be found perfectly unelectrified; Repeat the approach of the

excited glass rod, and whilst it is retained in its situation, separate the hemispheres by the removal of one of them by means of the wooden foot, taking care that they remain insulated, and immediately withdraw the excited rod. It will then be found (by help of the electrometer) that each hemisphere is in an oppositely electrical state as represented by the letters N and P.

If whilst the insulated sphere (fig. 115) is rendered temporarily electrical by induction, it be touched for a moment by the finger, it will be found on first removing the finger, and immediately afterwards the inducing excited tube, that the globe now retains a negative charge, and will even give a spark, the positive electricity having been carried away by the hand, and not able, therefore, to return so as to reproduce the neutral state.

The subject of induction has been acutely studied, and successfully developed by Faraday (*Researches*, Series xi.) Before his researches the phenomena were presumed to depend upon an action taking place in straight lines through non-conducting media, the particles of the medium not being themselves affected: whereas it would appear from his experimental investigation of this extensive and intricate subject, that "induction is in all cases an action of contiguous particles, consisting in a species of polarity, instead of being an action of either particles or masses at sensible distances;" that it may be propagated not only in straight but in curved lines. Mr. Faraday's views have been so clearly abridged and illustrated by Mr. Daniell, that I shall, with his permission, avail myself of the following quotation and diagrams from his *Introduction*, in further illustration of this subject.

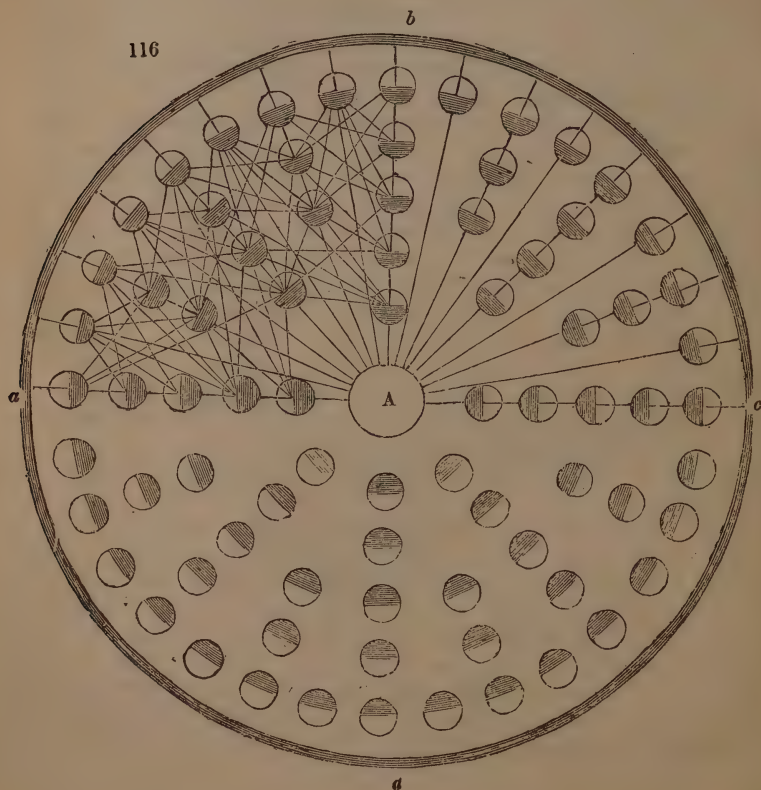
"We have seen," he says, "that one electric force cannot be produced without an exactly equal development of the other; and upon more attentive examination we shall find that no kind of matter, either conducting or non-conducting, is capable of receiving a charge in any way of one kind of electricity independently of the other, or without calling forth an equal amount of the opposite force in adjacent bodies. It was formerly supposed that the electric fluid was confined to the surfaces of bodies by the mechanical pressure of the non-conducting air, in the midst of which all our experiments are carried on; but the fact is, that the electric force originating or appearing at a certain place is propagated to, and sustained at, a distance, through the intervention of the contiguous particles of the air, each of which becomes polarized as in the case of insulated conducting masses, and appears in the inductive body as a force of the same kind exactly equal in amount, but opposite in its direction and tendencies.

"Such a forced arrangement of the molecules cannot be made to appear to the eye in the case of the air, but is established by the most perfect inductive reasoning; and a similar disposition may actually be exhibited by substituting a liquid non-conductor for the air under similar circumstances. If we take a tall, wide-mouthed glass vessel, and place it upon the prime-conductor of the electrical machine, taking care that there may be a good metallic communication through its bottom, and then fill it with spirit of turpentine containing some threads of white silk about one-eighth of an inch in length disseminated through it, they will be little

affected upon turning the machine till a metallic conductor is held near the surface of the liquid. Upon presenting, however, such a body, they will immediately erect themselves, and, collecting from all parts, will attach themselves to each other end to end, and form a continuous chain from the conductor to the exterior metal, towards which they will always incline as it is moved in different directions. These particles will adhere together with considerable force, as may be felt by touching them with a rod of glass; but the moment the conductor is discharged, they fall upon their sides, and sink to the bottom. If, instead of silk threads, we occasion particles of gold-leaf to float in the spirit of turpentine, the resemblance will be perfect; for, on approaching them with a rod of metal, when the conductor is charged, they immediately start on end as if endued with life, assume the polar state, attract each other end to end, but owing to their perfect conduction, discharge their electricity by minute sparks.

“Now the solid threads of silk accurately represent the fluid particles of the spirit in which they float, or of the air which is interposed between a charged conductor and surrounding bodies, and obviously assume a polar state, exactly resembling that of insulated conductors in similar circumstances.

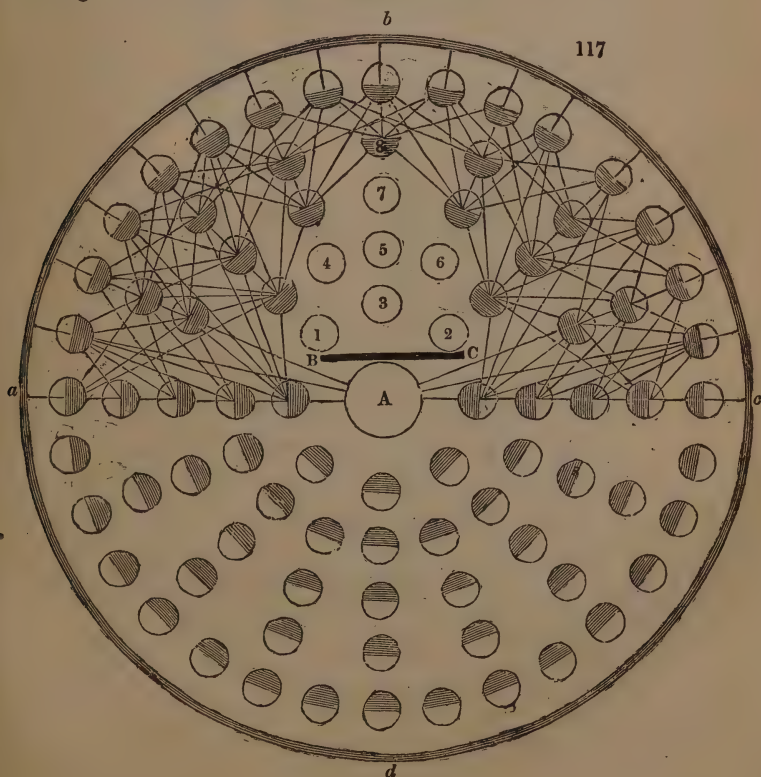
“In the annexed diagram (fig. 116), let A represent an insulated electrified



ball placed within an uninsulated metallic sphere, $a b c d$, filled with a non-conducting medium, whose particles are represented by the small included circles. These will be all thrown into a polar state, indicated by the shading, resembling the silk particles in the spirit of turpentine: their dissimilar poles will be all turned towards the ball A , and in this way their combined influence will be thrown upon the metallic sphere, $a b c d$, which will thus have a force of the opposite kind to that upon A , developed upon it, of exactly equal amount, but diffused over the larger surface. It is conceived that the polarized particles are capable of affecting each other, not only in straight lines as in the quadrant $A b c$, but in lines diverging from their centres, as shown in the quadrant $A b a$.

"Each polarized particle is in active relation, not only to a line of particles in some definite direction from it, but to all those which are contiguous to it. Hence, there is a lateral diffusion of force, and the lines of inductive action, when unobstructed, tend to spread as from a centre; or may assume a curved direction when any obstacle opposes their free radiation.

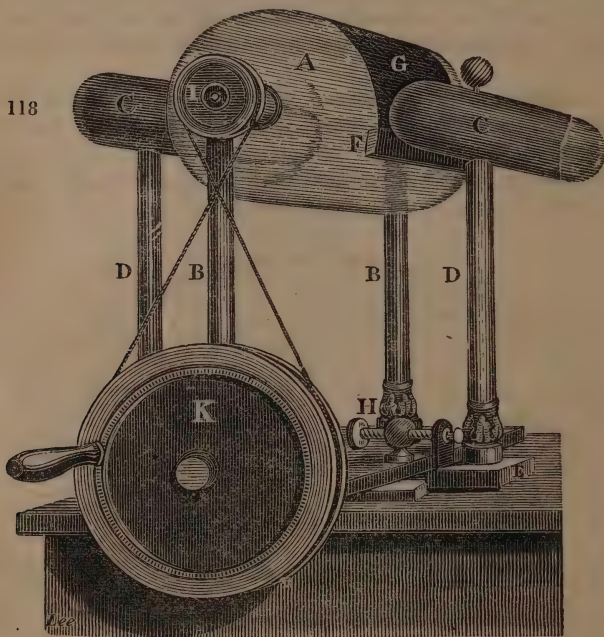
"In consequence of the lateral action of the particles upon one another, if $B c$ (fig. 117) be an obstacle interposed in the course of the induction from A to $a b c d$, the particles 1 2 3 4 5 6 7 will be protected from the influence, but the induction will affect the particle 8, by the bending of the lines of force on each side of it.



"The particles 1 2 3 4 5 6 7 themselves, although here represented in their natural state, will be affected by a reflex action; but will be polarized to a much lower degree than those within the influence of the direct action."

§ 5.—ELECTRICAL MACHINES.

IN the preceding details we have availed ourselves of the simplest apparatus, in order to explain the leading and principal laws of electrical excitation; all the experiments are easily made, and their results include some of the most important facts connected with the subject, to which, in the sequel, it will be necessary frequently to recur. For the further practical prosecution of these experiments, an *electrical machine* is indispensable; this, therefore, we may now proceed to describe.



The best electrical machine for experimental purposes, and for the general use of the student, is represented in the following wood-cut. It is commonly called *Nairne's machine*. (See fig. 118.) It consists of a *glass cylinder* A, about 10 or 12 inches in diameter, and 15 to 20 inches in length, turning between two upright pillars of glass, B B, fixed to a stout mahogany base. Two smooth *metal conductors*, equal in length to the cylinder, and about one-third of its diameter, C C, are placed parallel to it upon two glass pillars D D, which are cemented into two sliding pieces of wood E, by which their distance from the cylinder may be adjusted. One of the conductors has a *cushion*, F, attached to it (by a bent metallic spring) nearly as long as the cylinder, and about one inch or an inch and a half wide, to the upper part of which is sewed a *flap* of

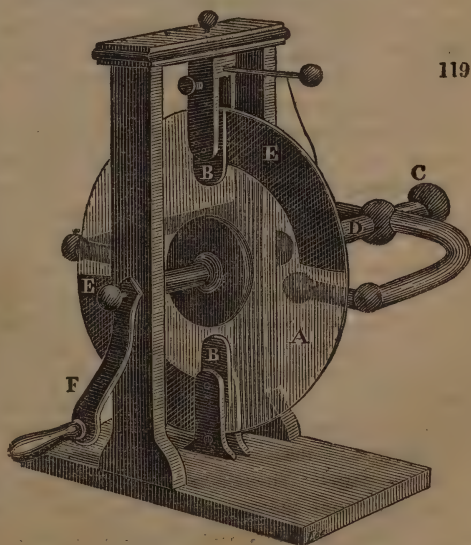
silk, *G*, which should reach from the cushion over the upper surface of the glass cylinder, to within about an inch of a row of points attached to the side of the opposite conductor. The conductor to which the cushion is attached is called the *negative* conductor; the other collects the electricity of the glass, and is called the *positive* conductor: *H* is an adjusting screw to regulate the pressure of the cushion upon the cylinder. The motion of the cylinder is in the direction of the silk flap, and may be most simply communicated by a handle attached at *I*, or, if necessary, by the multiplying wheel *K*. It is obvious, that in this form of the electrical machine, the cylinder and the cushion correspond to the glass tube and silk rubber employed in the former experiments, and that all the phenomena appertaining to the excited *tube* will be exhibited by the cylinder *A*, and the conductor opposed to it, whilst those of the excited *silk* or rubber, will belong to the cushion *F*, and to its conductor.

To put this electrical machine into good action, every part should be made *perfectly clean and dry*. The cushion is then anointed with *amalgam*, and applied by a gentle pressure to the cylinder. If *positive* electricity is required, it may be received from the conductor bearing the points, that supporting the cushion being, at the same time, uninsulated by an attached wire, passing from it to the stand; if, on the contrary, *negative* electricity is required, it may be obtained from the insulated cushion and its conductor, the other conductor being uninsulated.

The best *amalgam* is composed of one part of tin and two of zinc melted together, and mixed, while fluid, with six parts of hot mercury in an iron mortar. This mixture is triturated till it becomes a fine powder, which is then formed into a tenacious paste with hogs' lard.

Another form of the electrical machine, usually called the *plate machine*, consists of a circular glass plate *A* (fig. 118), mounted upon an axis, and rubbed by two pairs of cushions, as shown at *BB*. The brass conductor *C* has its points opposed to the plate, and is insulated by the glass stem *D*: *EE* are double pieces of oil-silk passing from the cushions to near the points. The whole is supported by a stout mahogany frame, and motion is given to the plate by the winch *F*.

These electrical machines have considerable power; they are easily cleaned and excited, and are more portable than the cylinders; but as they cannot be conveniently insulated, the negative electrical power cannot be so well exhibited; for the general purposes therefore of experimental illustration, the former machines are preferable.



When either of these electrical machines have been for some time out of use, they require to be thoroughly cleaned: for this purpose, the conductors and cushions must be removed, and the cylinder or plate cleansed with a little whiting and spirit of wine; it must then be wiped perfectly dry with a clean, warm, and soft cloth. It is a common custom to set the machines before the fire, but this is apt to soften their cemented joints, and endangers the plate or cylinder; the former especially is often cracked by incautious warming, and, in this case, the crack generally commences at the axis, and gradually proceeds towards the circumference; its progress may often be successfully checked by drilling a hole through the plate at the point of the crack. *Dryness* rather than warmth of the air is requisite for the activity of the electrical machine; it should, therefore, be kept in a dry room. When the glass parts of the machine are perfectly clean and dry, the cushions, freshly amalgamated, may be applied; their pressure upon the cylinder or plate should be very moderate, and they also should be dry and warm. The brass parts of the machine and of other electric apparatus are very commonly lacquered, which ought not to be, as it often interferes with their uses: the brass knobs especially should be clean and polished, but not varnished*.

§ 6.—GENERAL PHENOMENA OF ELECTRICITY OF TENSION.

WHEN the electrical machine is in good order, and the atmosphere dry, it produces a *crackling noise* when the plate or cylinder is turned, and flashes and *sparks of light* are seen upon various parts of the glass, passing from the cushion to the conductor: if the knuckle be held near the conductor, sparks pass to it through some inches of air, with a peculiar noise, and excite a slightly-painful sensation in the part upon which they are received. These, and the other phenomena we may now notice, are especially characteristic of electricity of *tension*.

It is conjectured that the cause of the *spark* thus perceived is the sudden compression of the air or medium through which the electricity passes, and it is always probably attended by a proportionate *elevation of temperature*, as is shown by the power of the spark to inflame spirit of wine, and some other easily inflammable compounds.

In these electrical machines the surface of the glass becomes positive by friction upon the rubber or cushion, which becomes negative; and as the cylinder or plate is kept in progressive motion, it follows that, provided there be a means of carrying off its positive electricity, it will continually receive a new supply from the uninsulated rubber; if, on the contrary, no means of conducting it away be resorted to, it will perpetually annihilate itself by retransmission to the cushion. But when the cushion is insulated, the abduction of electricity must be very limited: hence, to the full and perfect operation of the electrical machine, two circumstances must co-operate; there must be a means of withdrawing the generated electricity from the surface of the glass, and of preserving the supply to the cushion: of these, the former is effected by the opposed prime conductor; the latter, by connecting the cushion by a metallic chain or wire

* There are several splendid electrical machines of large dimensions and great power, at the Royal Institution; among them, one of two plates of four feet diameter each, revolving upon the same axis.

with the earth. We accordingly observe, in examining the operation of the electrical machine,—1st. That the electricity in either conductor is extremely feeble when they are both well insulated. 2ndly. That when one conductor is uninsulated, the power of the other is proportionately augmented; in the positive conductor, because then the other draws uninterrupted supplies from the earth; and in the negative conductor, because the positive freely transmits, and hence is left in a state rapidly to receive. 3rdly. That the cushion and the surface of the glass are always in opposite states. 4thly. That the negative and positive electricities excited, bear precisely that relation which enables them, when combined, to neutralize each other: in other words, that the *deficiency* of electricity on the one side is exactly such as to be restored by the *redundancy* on the other.

Those who advocate the hypothesis of two distinct electric fluids explain the action of the electrical machine as follows: they suppose that by friction the neutral electric fluid of the rubber is decomposed, the positive adhering to the glass, and the negative to the surface of the cushion; that the positive surface of the glass in its turn decomposes the neutral electricity of the prime conductor, the negative element of which is attracted by the positive of the glass so as to reproduce upon it the neutral state, whilst the prime conductor having thus lost negative electricity is left more or less highly positive, not by receiving electricity from the revolving glass, but by having parted with its own negative fluid to the glass.

The appearance of the *electric light* is modified by the density of the medium through which it passes. In common air, short sparks are straight, or nearly so, and long ones zigzag; the former are brilliant, especially at their extremities; the latter usually of a paler or redder hue. In condensed air, the electric spark is bright and white; in rarified air, it is of a reddish tinge, and faint and divided; in the more perfect vacuum of a good air-pump it is of a purplish hue, and only visible in a dark room. In a good Torricellian vacuum the light is faint blue; and in the most perfect vacua which can be obtained, it is scarcely visible, and of a greenish tint. In gases, the electric spark usually appears most brilliant in those which are most dense; in hydrogen gas, it is faint and red; in carbonic acid, it is vivid and white. It is also modified by the nature of the surfaces from and to which it passes.

By the aid of Nairne's electrical machine, all the phenomena of excitation, and of attraction and repulsion, may be very conveniently studied. The conductor attached to the cushion is *negative*, and that opposed to the cylinder *positive*; the former, therefore, represents the *sealing-wax*, and the latter the *glass*, employed in the experiments above described. If we attach two pith-balls to either conductor, they *repel* each other; but if one be attached to the negative, and the other to the positive conductor, they *attract* each other. If the two conductors be connected by a metallic wire or chain, all electrical appearances cease, showing that the negative and positive powers are exactly such as to *neutralize* or *annihilate* each other: and in this case, a current of electricity traverses the wire, passing from the positive to the negative conductor; and, when a break is made in it, a succession of sparks pass between the divided extremities. This

wire, during the passage of the electricity through it, exhibits other and most important properties, which we shall afterwards have to advert to.

Whenever a spark passes, it announces the annihilation of the opposite electrical states, they having been previously brought into existence by induction. The knuckle held near the positive conductor becomes negative; and when the opposite states have acquired a certain degree of intensity, a spark passes, and the state of excitation is at an end.

There is an important circumstance attending the distribution of quiescent electricity, which is, that it belongs to surfaces only, and is so far independent of quantity or mass of matter, that a hollow sphere receives the same charge as a solid one. Coulomb found that an excited globe of metal afforded no indication of electricity in its interior; and that an excited hollow cylinder, open at the ends, imparted no charge to a small insulated disc, introduced into, and brought into contact with, its interior. The following illustration of the same fact is due to Biot. He suspended a metallic sphere by a silk thread, and exactly covered it by two moveable thin metallic hemispheres, which, by insulating handles, could be applied and removed at pleasure. On communicating a charge to this sphere *with* its exterior coating, he found, upon its removal, that the whole of the charge was carried away upon it, and that the sphere remained without electricity: and again, on charging the sphere, and then applying the coating, the whole of the electricity manifests itself upon the latter, and may again be carried away as before. This experiment requires some dexterity in its performance, but is perfectly satisfactory in its results. In the same way, if any metallic vessel, such as a pail or pot, be insulated and charged with electricity, on bringing an insulated carrier-ball to its exterior, electricity may there be carried away and communicated to a gold-leaf electrometer; but on applying the carrier-ball, carefully to its interior, it will not receive a trace of electricity. The cause of this apparent paradox will be evident by a reference to Mr. Daniell's diagrams. Thus, if we suppose $abcd$, (fig. 116,) to be a hollow sphere charged with electricity, an insulated ball, a , introduced into and touching any part of its interior could receive no charge, "because, being surrounded by a surface in one electrical condition, it could not induce the opposite state by polarising the surrounding air, by which alone a charge could be sustained: this will be at once obvious by supposing the ball, a , shaded the same as the circle, $abcd$, to denote a similar state of electricity, when the polarised state of the particles represented in the diagram will be seen to be impossible."

It has been concluded that in a solid body, having the form of a sphere, the electric fluid is accumulated in a very thin stratum at its surface, and everywhere equally, so that a spark, taken from any part of the surface, is of equal length, and the electricity has not more tendency to escape from any one part than from any other; its *intensity*, therefore, is said to be everywhere equal. But if we alter the form of the surface, we at the same time alter this equal distribution of electricity. If two similar spheres be placed in contact, there will be two points of greatest and equal intensity on their opposite sides in a line with their point of contact, and at that point the electricity will be null. In an ellipsoid, also, the greatest accumulation appears at the *extremities* of the longer axis,

and there the *intensity* of the electricity is at its maximum, and increases with the length of the axis: so that if the ellipsoid be considerably elongated, the intensity is very feeble at the equator, and very great at the poles; and in cylindrical bodies, the greater the proportion of the length to the breadth, the greater will be the intensity at the extremities. Coulomb found that in a cylinder, 30 inches long, and 2 inches in diameter, the intensity of the electricity at the ends was to the intensity at the middle as 2·3 to 1. If the conductor be elongated into a point, the intensity there becomes so great as to draw to itself nearly the whole of the electricity; hence, wherever points project beyond the general surface, there is a tendency in the electricity to pass off. The tendency, therefore, of the electric fluid to pass off from surfaces, or in other words its pressure against the air, in the language of the mathematical electricians, is considered proportional to the square of its quantity: so that, if the electric accumulation at four different parts of a conductor be as 1, 2, 3, and 4, the pressure against the air at those parts will be as 1, 4, 9, and 16. These important influences of the forms of the surface have been well put by Mr. Daniell. "If two balls of unequal diameters be placed together, the maximum intensity of the extreme point of the smaller sphere will be higher than that of the corresponding point of the larger, and by adding a series of balls in contact with each other, all gradually decreasing in size, the intensity will increase upon the smaller as the diameter decreases. We can conceive a succession of such balls gradually diminishing till the series ends in a mere point, at which the electric tension will be at its maximum. In consequence of this law of distribution, a powerful dispersion of electricity takes place from all bodies of a pointed form, the intensity upon them increasing to such an extent that the surrounding insulating medium of air gives way before it, and no longer suffices to restrain it."

§ 7.—ILLUSTRATIONS OF ELECTRICAL ATTRACTION, REPULSION, AND INDUCTION, AND OF THE INFLUENCE OF POINTS.

THE statement of facts respecting electrical attraction, repulsion, and induced electricity, admits of many elegant and amusing illustrations by the electrical machine; the apparatus for which, with instructions for its use, will be found in the repositories of the philosophical instrument makers.

The *head of hair*, which stands on end when electrized, serves to illustrate the direction of the lines of induction, each hair, as if repelled by its neighbour, radiating towards the nearest point in an oppositely induced state, and consequently converging towards the finger when held near them. A similar experiment may be made by placing a person upon an insulated stool, in connexion with the conductor of the electrifying machine; his hair will diverge as in the above figure.

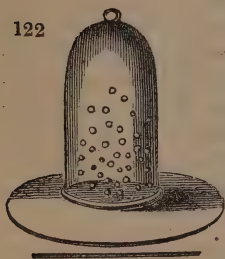


The following is a sketch of the simplest form of the *electrical peal*



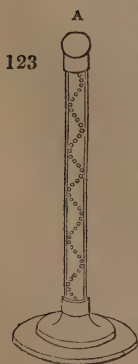
of bells, which ring by the attractions and repulsions of small clappers suspended between them. The bells are arranged as follows: *a* is a brass hook and wire by which they are suspended to the conductor; *b* the bells attached to the wire by a brass chain, the centre one being suspended by silk; *c* the clappers also suspended by silk. The electricity received at *a* is slowly dissipated by the edges of the bells, the ringing of which is occasioned by the alternate attractions and repulsions of the insulated clappers. A better arrangement consists in suspending the central bell by silk in the same way as the clappers, and connecting it with the table by the wire *c*.

Dancing figures, cut out of light paper, may be made to exhibit very ridiculous movements by a little management in turning the machine. For this purpose, suspend a brass plate from the conductor of the machine, and beneath it, at the distance of four or five inches, place a similar brass plate connected with the ground; on this put the paper figures; when the upper plate is electrified, they rise and perform a dance by their motion between the plates.



A good experiment, illustrating attraction and repulsion, consists in attaching a wire, with a blunt point, to the prime conductor, and holding over it a clean dry bell-glass, the interior of which will thus receive a superficial charge; if it be then set upon the table over a dozen pith-balls of different sizes, they will dance up and down in it for several minutes, until they have nearly carried off its redundant electricity.

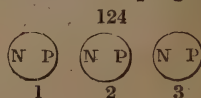
Among the experiments particularly illustrative of electrical induction, we may notice the *luminous tubes* and *words*, in which a number of



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sparks are made to pass between small pieces of tin-foil, so arranged as to produce in a darkened room a variety of figures and devices. In the *luminous tube*, a number of small spangles of tin-foil are pasted spirally round a tube about half an inch in diameter, and within a very short distance of each other; upon holding the brass-ball *A* to the prime conductor of the machine when in good action, the other end of the tube being uninsulated, a beautiful succession of small sparks is seen between each of the little discs of foil. The opposite electrical states are here produced by induction throughout the series of spangles, the passage of the sparks indicating the momentary annihilation of the electricities. Let the following figures, for instance (fig. 124), represent three of the discs or spangles:

it follows, then, that 1, being held near to the positive conductor, will become *polar*, as represented by the letters *N* and *P*: and the



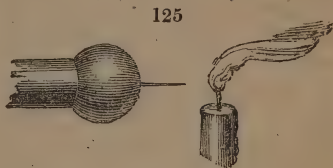
124

whole series, whatever may be their number, will be thrown into the same state as the conductors represented in the figure at page 249, and remain so till the spark passes.

The influence of points in receiving and carrying off electricity has already been adverted to, and may be further elucidated by the following experiments. If we hold a pointed wire to the prime conductor, it rapidly and silently draws off its electricity, and sparks cannot be taken from it by the knuckle, or a brass ball, while the point is in its neighbourhood; or if we attach a pointed wire to the conductor, there is the same convection of electricity; and on holding the hand near the point, we perceive a peculiar coldness, or wind, as it were, which has been called the *electrical aura*: it is even sufficient to blow out a candle held near it. This arises from the secession of the electrified particles of air in consequence of the inductive force concentrated upon the point.

If the point itself be moveable, it will of course be itself reacted upon, and upon this principle a variety of ingenious apparatus has been constructed, such as *fly-wheels*, *orrieres*, and so on. A simple instance is shown in the annexed cut (fig. 126), in which a *fly* with four arms, each terminating in a point at right angles to the arm, is balanced at its centre upon a pointed wire stuck into the prime conductor. The escape of the electricity from the points, and its action upon the adjacent air, causes the fly to revolve rapidly.

If these experiments be made in the dark, it is observed that a point held towards the *negative* conductor has the appearance of giving out a *brush of light* (fig. 127); but when held to the *positive* conductor, a *luminous star* or point is all that is observed (fig. 128). These appearances have been supposed to demonstrate the existence of an *electric fluid*, which, in the one instance, is supposed to be *escaping from*, and, in the other, *received by*, the point: but these affections of light cannot be admitted as proofs of the existence of any distinct form of matter*.



* The philosophy of the electric discharge by sparks, brushes, &c., has been minutely studied and ably illustrated by Mr. Faraday, more especially in the 12th series of his *Researches*; he has also described its appearance in various media or dielectrics; his details upon these subjects are extremely curious and important, but are too extended to be here quoted, and scarcely admit of such abridgment as to bring them within my

limits, I must, therefore, content myself by referring the reader to the original. It will be observed that the brush differs from the spark in being "a discharge between a bad or a non-conductor, and either a conductor or another non-conductor; the spark ensues where an insulating dielectric is interposed between two conducting surfaces in opposite states of electricity; and then if the actions be continually increased in strength, or

§ 8.—OF INDUCTION THROUGH GLASS, AND OF THE LEYDEN JAR.

FROM what has been said respecting *induced electricity*, and the electrical accumulation dependent upon it, it will appear that the intervention of conductors and non-conductors, or imperfect conductors, is requisite to the existence of the phenomena. In the cases cited, the non-conducting medium through which it takes place, or the dielectric, is the *air*; we shall now show that induction may also take place through *glass*.

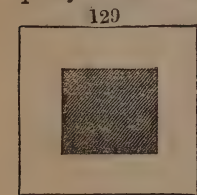
For this purpose it is only necessary to excite one side of a clean, dry pane of glass, by rubbing it with a piece of silk; and, on holding a feather or pith-ball to the other side of the pane, it also will be found electrical. If we now examine the nature of the electricities by which the glass plate is charged, it will be found that the rubbed side being *positive* the opposite side is *negative*.

In the same way we may charge a plate of glass with the opposite electricities, by holding it to the prime conductor of the machine: in this case sparks will often appear to pass through the glass; but, on removing it, the side which has *touched the conductor* will be found *positive*, and the opposite side *negative*.

As glass is a non-conductor, it is difficult to spread the electricity equally over its surface: this, however, may easily be effected by coating both sides of the pane with thin tin-foil to within about an inch and a half or two inches of the edge, as shown in fig. 129. If we now communicate electricity to one side of the plate, the other, not being insulated, will become oppositely electrical, and in this way a *charge* will be acquired by the plate: if we now, by means of a bent wire, make a communication between the two sides of the coated pane, a

bright spark will pass, and the accumulated electricities will be immediately annihilated.

We avail ourselves of arrangements of this sort for the purpose of accumulating electricity, which may thus be accomplished to a great and powerful extent; but the pane of glass is an inconvenient form of apparatus for the purpose, and we usually substitute for it a phial or jar, as represented in fig. 130, coated inside and out with tin-foil to within three or four inches of its mouth. A brass wire, surmounted by a knob, is then made to communicate with the interior coating, and the apparatus is ready to receive its charge of electricity, precisely upon the same principle as the pane of glass. This is called the *Leyden jar or phial*, the method of arrangement having been accidentally discovered in 1700 by Muschenbrock, of that University. The glass should be thin, and, as far



otherwise favoured, either by exalting the electric state of the conductors, or bringing them nearer each other, or diminishing the density of the dielectric,

a *spark* at last appears, and the two forces are for the time annihilated, for the discharge has occurred."

as possible, uniform throughout; for phials or jars which are very thick, or much thicker in one place than another, are unfit for the purpose.

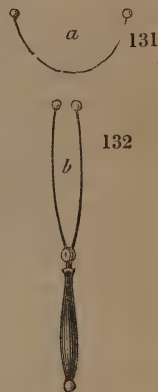
If we now hold the jar by its outer coating, and present the knob near to the conductor of the machine, a succession of sparks will pass into it, at first very rapidly, afterwards more slowly, and at length ceasing altogether. The jar is then *charged*; and if a communication be now made by a metallic wire, from the outer to the inner coating, a bright spark, attended by a snapping noise, will pass from the knob, after which no further effect will be produced, the jar having been *discharged*. The jar may also be charged by receiving the sparks upon the outer coating, whilst the knob is held in the hand.

The wire used for the above purpose should be mounted with balls at its ends, and is usually called a *discharger*, *a*; it is sometimes *jointed*, for the convenience of applying it to large and small jars, and mounted upon a glass handle, *b* (figs. 131, 132).

If, having charged the jar, and holding its exterior coating in one hand, we touch the knob with the other, the spark passes as before, and we perceive a peculiar and very painful sensation at the wrist and elbows, and across the breast, which is called the *electric shock*. It is painful for the moment only, and leaves little other permanent impression than that resulting from fear or surprise.

In charging the jar as above described, if we keep it in contact with the conductor, and the machine is in good action, we observe, after a time, that flashes of light pass across the uncoated interval, which are soon followed by a loud crack or explosion, and a long and brilliant spark passes from the wire to the coating. In this case the electricity has been accumulated to such a degree of intensity as to discharge itself spontaneously over the exterior uncoated interval.

To ascertain the relative charge which the jar has received, and its power of retaining that charge, we employ the *quadrant electrometer*, (fig. 133,) contrived by Henley. It consists of a round stem of metal, seven or eight inches long, surmounted by a ball, to which is attached a semicircle, most conveniently made of thin ivory: in its centre a pin is fixed, on which a slender slip of cane, about four inches long, with a pith-ball at its other end, turns freely, and traverses the semicircle as an index; the lower half of the semicircle is divided at the edge into ninety degrees. When this instrument is electrified, there is, of course, a tendency to repulsion between the moveable ball and the stem: the ball therefore recedes, and carries the index over the graduated circle, to a greater or less extent, in proportion to the intensity of the electric charge. The repulsion is at its maximum when the index stands at right angles to the stem, or at 90° upon the scale. This electrometer may be fixed upon the prime conductor, or upon the knob of the jar. The latter is often a very convenient place for it,



because, having charged the jar and removed it from the conductor, we see by the behaviour of the electrometer how far the jar retains its charge.

There are many other electrometers which are applicable to these high charges of electricity, among which Cuthbertson's *Balance Electrometer*, and Lane's *Discharging Electrometer*, will be found very useful. Mr. Harris, of Plymouth, has also described a balance electrometer, (*Phil. Trans.*, 1834, p. 213,) by which the mutual attraction of oppositely electrified surfaces may be very accurately estimated and compared; and in experiments in which it is required to charge Leyden jars or batteries with known proportions of electricity, the *unit-jar*, contrived by the same electrician, is also a most useful piece of apparatus.

In charging the Leyden jar many hundred sparks are observed to enter it, which, when it is discharged, are all concentrated into one; hence the brilliancy of its light, the loudness of the explosion, and the acuteness of the sensation which it produces.

When the jar is in direct communication with the conductor of the machine, it diminishes the intensity of its electricity, and consequently admits of a greater change in its electric state before any given resistance is overcome, or force of attraction manifested. This is shown by attaching the quadrant electrometer to the conductor of the machine, which, when turned, immediately causes it to rise to its full extent; but when the interior coating of the jar is in union with the conductor, the machine must be turned for some time before the rise of the electrometer attains its maximum.

The *annihilation* of *positive* by *negative* electricity, and the reverse, may be strikingly shown by attaching the quadrant electrometer to a Leyden jar, and giving it a certain charge—say to twenty degrees—from the *positive* conductor; then transfer it to the *negative* conductor, and whilst apparently receiving a negative charge, the electrometer will gradually fall, and, at length, all electrical accumulation disappear: then, as the jar acquires its negative charge, it will again rise, and may be again discharged by transferring it to the positive conductor.

The power of the Leyden phial, as a source of electrical accumulation, being dependent upon the opposite states of its two surfaces, it is obvious that one of them must always be connected with the ground, in order that it may acquire its charge. If we suspend a jar by its knob (a thin globular jar answers best for this experiment) to the positive conductor of the machine, its outer coating, being surrounded by dry air, cannot give off any of its electricity, and consequently it will receive no charge so long as it remains thus insulated; but if we hold the hand near the outer coating, sparks of positive electricity will pass off, and the jar acquire a charge. This is a good experiment, illustrating the Franklinian theory of electricity, which supposes the electric fluid to be present in all bodies, but to manifest itself only when its equilibrium is disturbed. Thus, when we charge a jar in the usual way, we *add* to the electricity of its interior coating, whilst its exterior *throws off* an equivalent quantity: so that the former becomes *positive*, or *plus*, and the latter *negative*, or *minus*: but if the jar be *insulated*, the electricity cannot escape from the outer coating, and consequently the jar cannot be charged. The theory of two

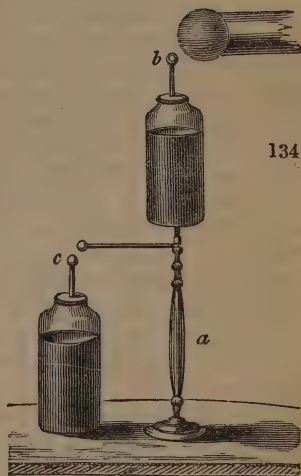
fluids assumes that the positive electricity deposited upon the inner surface of the jar repels the positive electricity from the outer surface of the jar, and attracts the negative electricity: that, therefore, every spark which passes from the conductor to the knob, occasions an increase of positive electricity upon the inner surface, and of negative electricity upon the outer surface, and that the mutual attraction between these two electricities prevents their spontaneous escape, and occasions a greater accumulation of each upon their respective surfaces: that when a communication by a perfect conductor is made between the two surfaces, the electricities rush into combination, and all appearances of accumulation or excitation are at an end.

The following experiment further illustrates this subject:—Take two Leyden jars of similar size (fig. 134); insulate one of them by fixing it upon a glass stand, *a*, and place the other on the table, with its knob half an inch distant from the coating of the insulated jar, the knob of which should be placed at the same distance from the conductor of the machine. For every spark that passes to the knob of the first jar, *b*, there will be a similar spark pass *from* its coating to the knob of the second jar, *c*, and both jars will become *similarly* and equally charged. As, therefore, the second jar is thus charged by sparks emitted from the exterior surface of the first, and as their charges are equal, it follows that for every portion of electricity *added* to one side of the coated glass, a corresponding or equivalent portion *leaves* the opposite surface.

The preceding wood-cut shows the proper arrangement of the apparatus for this experiment.

Upon this principle *a jar may be charged by the transfer of its own natural electricity from one surface to the other*: for instance, suspend a jar to the *positive* conductor of Nairne's machine, and connect its *outer* coating by a wire with the *negative* conductor or rubber, the whole being in a state of insulation, so as to prevent the access of electricity from the earth. A few turns of the machine will charge the jar; that is, the electricity which is thrown *into* its inner surface by the positive conductor, is abstracted *from* its outer surface.

This experiment is further instructive, as showing the *impermeability of glass to the electric fluid*, for the conductor and the rubber of the machine are separated from conducting contact with each other by the thickness of the glass jar only, and a considerable accumulation of electricity takes place, which the contact of the thinnest film of conducting matter, or the slightest fissure in the glass, would effectually prevent. When the glass of the Leyden jar is very thin, it does occasionally happen that it is perforated by a powerful charge; in this case a small round hole is observed in the glass, and the jar is rendered useless.



It has been said above, that a plate of glass not covered by tin-foil, may be charged by contact with the prime conductor: *the metallic coating, therefore, is not essential to its charge*, but its principal use is, by its conducting power, to spread the electricity over the surface of the glass, and to enable it, when the discharge is made by uniting the opposite surfaces, to be carried off *at once* in a single spark. Jars are sometimes made with moveable coatings; these may be charged as usual, and the coating removed and again replaced, when it will be found that they still retain their electricity, which appears to adhere to the surface of the glass.

Mr. Faraday's researches have disclosed new views respecting the extraordinary condition of the glass, or of the molecules of the glass in a charged jar, and as constituting the polar *dielectric*; each layer of particles being, as he assumes, thrown into a peculiar polar condition, which, if retained, constitutes insulation, but which, if lowered by the communication of power from one particle to another, constitutes conduction: he regards insulation and conduction as only extreme degrees of one common condition or effect, and shows that these two apparently perfectly dissimilar conditions may be associated by numerous intermediate links.—(See Series xii. of his *Researches*.)

The following experiment to a certain extent illustrates the condition of the charged glass in the above experiments; if we apply to particles what we here observe in regard to masses. Apply the uncoated sides of two thin plates of glass, each coated upon one side only, to each other, and charge them; on attempting to separate them they are found to adhere together, and, on separating them, the uncoated side of the plate which had touched the conductors will be found positive, and that of the other negative.

Mr. Faraday's views of the nature of induction led him to infer the existence of a *specific inductive power* peculiar to each substance, and he proved it by very decisive experiments (*Researches*, series xi.), in which, among other forms of apparatus, he employed what he has termed a *differential inductometer*, one of the forms of which consisted of two insulated brass plates placed within a certain distance of each other, one of which was connected with the cap of a gold-leaf electrometer: on electrifying the other, it acted by induction through the air upon the electrometer, and produced a certain extent of divergence of the leaves: plates of different substances were then substituted for the air interposed between the plates, and the divergence was either increased or diminished, according to the relative facilities with which induction took place through the interposed substances: he thus ascertained that the specific inductive capacity of air being assumed as = 100, that of glass is = 176, of shell-lac = 200, and of sulphur = 224. With respect to aëriiform bodies, he ascertained the curious fact that they all possess the same power of sustaining induction; no variations either of their density or elasticity produced any change in the electric tension, till rarification was carried so far as to enable the discharge to take place across them; hot and cold, and dry and damp air were compared, but no difference was observed.

In speaking of the different states of electricity, the terms *quantity* and *intensity* are frequently used to indicate the different phenomena which it exhibits: the former implies the actual quantity of electricity in any body;

and the latter, or the term *tension*, signifies the state of electricity indicated by the electrometer, and its power of flying off from surfaces, and passing through a certain stratum of air or other ill-conducting medium. The meaning of these terms will be more evident when we are considering the electricity of voltaic combinations: in the mean time, as regards the electricity of the machine, they may, perhaps, be further illustrated as follows:—If we suppose a charged Leyden phial to furnish a spark, when discharged, of one inch in length, we should find that another uncharged Leyden phial, the inner and outer coating of which were communicated with those of the former, would, upon the same quantity of electricity being thrown in, reduce the length of the spark to half an inch; here, the *quantity* of electricity remaining the same, its *intensity* is diminished by one-half, by its distribution over the larger surface. Upon the same principle, if a long metallic riband be coiled up and placed upon the cap of a gold-leaf electrometer, the leaves of which are fully diverged by a sufficient charge of electricity, it will be found upon uncoiling the riband by means of an attached silk thread, so as still to preserve insulation, that the leaves collapse to a greater or less extent, in proportion to the quantity of the riband uncoiled, and that, upon allowing it again to coil up, they again diverge; here the extent of the divergence is proportionate to the intensity of the electricity, which, the quantity remaining the same, is increased or diminished inversely as the surface exposed.

It is obvious, that the *extension of surface* will be attended with a greater superficial exposure to the unelectrified air; and hence it might be expected, that a similar diminution of intensity would result from the vicinity of the electrified surface to the ground, or to any other body of sufficient magnitude in its ordinary or unexcited state. That this is the case, may be shown by diverging the leaves of the gold-leaf electrometer, and in that state, approaching the instrument with an uninsulated metallic plate, which, when within half an inch of the electrometer-plate, will cause the leaves to collapse; but on removing the uninsulated plate, they will again diverge, in consequence of the electricity regaining its former intensity. The same fact is shown by the *condensing electrometer*.

The influence of the air upon the retention of electricity by surfaces has already been mentioned, and may be further illustrated by the Leyden phial, which, if charged, and placed under the receiver of the air-pump, gradually loses its charge during exhaustion, and if the experiment be made in the dark, the two electricities are seen annihilating each other by flashes of light. This tendency of electricity to fly off from surfaces, is always greater in rare than in dense media, and consequently the length of the spark, or *striking distance*, (as when a charged jar is discharged,) supposing the *quantity* of electricity to remain constant, will vary, inversely as the density of the air; and, according to Mr. Harris, the resistance to the passage of the charge varies as the square of the density of the air; and Dr. Turner found the striking distance for the same charge greater in hydrogen than in air, and greater in air than in carbonic acid gas. If electricity, though of great intensity and small quantity, be made to pass through a non-conducting medium, its effects are curiously increased; and in this way it may be made to perforate glass; as when we surround

a pointed wire by wax or oil, and take sparks from it through a thin phial. The passage of electricity through air of different densities, and in vessels and tubes of different shapes, lengths, and diameters, gives rise to a number of beautiful and very interesting experiments. The good conducting power of flame, and the facility with which it discharges electricity, may also probably be referred to its rarity. But all these phenomena, and others which have been more exclusively referred to the air's pressure, are principally referable to changes in the inducing power of the dielectric, or surrounding medium, and are beautifully consistent with those views of the nature of specific induction which Mr. Faraday has deduced from his experimental researches (Series xii.). In reference to the pressure of the atmosphere, as influencing the retention of electricity upon the surfaces of conductors, Mr. Faraday well remarks, that "it associates two such dissimilar things as the ponderous air and the subtle and even hypothetical fluid or fluids of electricity by gross mechanical relations; by the bonds of mere static pressure. My theory, on the contrary, sets out at once by connecting the electric forces with the particles of matter; it derives all its proofs, and even its origin, in the first instance, from experiment; and then, without any further assumption, seems to offer at once a full explanation of those and many other singular, peculiar, and, I think, heretofore unconnected effects."

The Leyden jar furnishes a striking illustration of that case of induction before alluded to (p. 258), in which the two electric forces are so limited in their direction as to present no indications external to the apparatus employed; thus if we charge a jar, and then, by an insulated handle or silk thread, remove the charging ball and wire, such jar will present no electric appearances on examining either coat by an insulated carrier-ball; if such a ball having been in contact either with the inner or outer coat be examined by the gold-leaf electrometer, no signs of electricity can be detected: the two forces are confined to the coatings, or to the particles of the dielectric contiguous to them, and are entirely engaged to each other by induction through the glass. But if we now replace the charging-ball and rod, by an attached silk thread, then the part projecting above the jar will give a powerful charge to the carrier-ball, and the outside coating of the jar, if it be insulated, will be found in the opposite state; each strongly inductive to surrounding objects; and after these trials, on discharging the jar, we have evidence, by the usual phenomena, of the annihilation of the previous inductive state.—(FARADAY, Series xiv., § 1682.)

The power of the Leyden jar, in receiving and retaining electricity, is proportioned to its surface, but a very large jar is inconvenient, and difficult to procure; the same end is attained by arranging several jars, so that by a communication existing between all their interior coatings, their exteriors being also united, they may be charged and discharged as one jar. Such a combination is called an electrical *battery*, and is useful for exhibiting the effect of accumulated electricity.

The discharge of the battery is attended by bright light, and by a considerable report, and if it be passed through small animals it kills them; if through fine metallic wires, they are ignited, melted, and burned; and gunpowder, cotton sprinkled with powdered resin,

and a variety of other combustibles, may be inflamed by the same means.

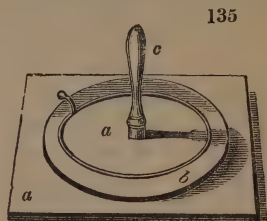
The mechanical force that accompanies the electric discharge is shown by the perforation of paper, the tearing of the leaves of plants, and of pieces of wood, and the breaking of plates of glass, through or over which it is made to pass; chemical decompositions may be effected by it, and it produces magnetic effects consistent with the laws which we shall afterwards point out*.

We observe, therefore, that certain attractive, repulsive, and inductive powers belong to electricity in a quiescent state, and that when in motion, it produces heat, light, chemical effects, and magnetism.

§ 9.—OF THE ELECTROPHORUS, AND CONDENSER.

THE *electrophorus* (fig. 135) is often used as a permanent source of electricity, and may sometimes be conveniently and economically substituted for the electrical machine, especially in the chemical laboratory. It consists of two *metallic* plates, *a a*, with an intervening plate of *resinous* matter, *b*; for the latter equal parts of shell-lac, resin, and Venice turpentine are generally used, the mixture being carefully melted in a pipkin, and poured, whilst liquid, into a wooden or metal hoop, of a proper size, placed upon a polished surface of glass or marble, from which it easily separates when cold; it should be about half an inch thick, and the smooth surface being uppermost, the lower side should be covered with tin-foil, or attached to any other metallic plate; a polished brass plate, with a glass handle *c* attached to it, is then placed upon the upper surface of the resinous plate, and of rather smaller diameter. The resin having been previously excited by gentle friction with a piece of dry fur, the instrument will be found to exhibit the following phenomena.

Upon raising the brass plate by its insulating handle, it will be found very feebly electrical; replace it, touch it with the finger, and again lift it off by its handle, and it will give a spark of *positive* electricity. This process may be very often repeated without fresh excitation, which circumstance, as well as the nature of the electrical charge, shows that the elec-



* The intensity of the heat produced even by the common electric spark, is such as easily to inflame alcohol, kindle gas flames, and so on; the reason why this heat is not, in common cases, observed, is the excessive rapidity of the effect, of which, as appears from Mr. Wheatstone's experiments, the term *instantaneous* gives us but a very imperfect idea; hence it is, that the spark taken from the hand *has not time to burn*, though a succession of sparks limited to the same spot produces inflammation; and we shall afterwards find,

that by diminishing the rapidity of the progress of electricity, or using a continuous current, we get a variety of effects *completed*, of which, the excessive transiency of the common electric spark either from the machine or Leyden jar, prevents the accomplishment. Any continuous current of electricity, which we can obtain by the common machine, is extremely small in *quantity*, hence the difference between its effects and those which we shall afterwards witness in other cases of electric excitation.

tricity of the moveable brass plate is not *directly* derived from the resin, but that it depends upon *induction*: this is more obvious by considering the upper plate, not as in absolute contact with, but merely very near the resinous disc, which, from the minute irregularities upon its surface, is really the case; the negative electricity, therefore, of the excited resinous plate, is communicated from a few points of contact to the brass plate, upon its first application, and then, the latter is precisely in the state of a conductor opposed to, but not touching, an electrified surface; and consequently in due condition to be rendered permanently electrical by induction, when occasionally uninsulated by the contact of the finger.

With this instrument, one phenomenon of induction may be shown, which cannot be so well exhibited by any other; namely, the increased capacity, as it is sometimes called, for electricity, of the conductor under the influence of induction. The brass plate, when placed upon the resin, may be regarded as in a polar state; the lower surface near the resin being *positive*, the upper surface being *negative*. Upon touching the upper surface with the finger, it instantly *acquires* electricity, loses its apparent polarity, and becomes positive, giving, upon removal, a positive spark to any conductor. It is obvious that in this case the brass plate represents one end of a conductor of indefinite extent. That the quantity of electricity received by the plate is equivalent to that given out, is supposed to be shown by the following experiment:—place the metallic upon the resinous plate, and touch the former with the knob of a Leyden phial; then touch the cap of an electrometer with the knob of the phial, and it will give a certain *negative* divergence to the leaves; raise the plate and present the knob of the jar to it, a spark will pass; and, upon applying the jar a second time to the electrometer, the leaves will entirely collapse, showing the exact annihilation of the former negative by the latter *positive* charge.

When the electrophorus is placed upon an insulating stand, its lower plate is always found in an opposite electrical state to the upper one, so that in this respect its plates resemble the coatings of a Leyden jar: it also well illustrates the great inductive capacity of the lac or resinous compound.

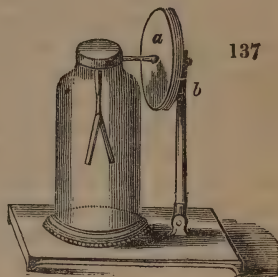
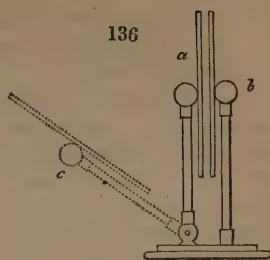
When an insulated surface is opposed to another which is not insulated, so as to be affected by it by induction, the electricity communicated to the former suffers an increase of tension on breaking the induction by removing the opposed uninsulated conductor: this property is exhibited as follows:—Provide a brass plate, three or four inches in diameter, and drop upon its lower surface three small spots of sealing-wax; place it upon a similar plate, forming the cap of the gold-leaf electrometer, from which it will be separated about a twentieth of an inch by the three small insulated legs of wax. Connect the upper plate with the ground, by touching it, and give a very feeble electrical charge to the electrometer, so as scarcely perceptibly to diverge its leaves; then suddenly remove the upper plate, by which the induction towards it will be broken, and the tension of the electricity suddenly increased, so as to cause a very considerable divergence of the leaves.

The plates employed in this experiment have been called *condensers*.

They are sometimes placed perpendicularly, as in fig. 136, and the uninsulated plate *a* is supported by a wire and joint, so as to be brought as close as possible to the insulated plate *b*, without touching; the latter is in communication with the electrometer, and having received its charge, the moveable uninsulated plate is drawn back, as in *c*, and the intensity of the electricity displayed.

Sometimes the condenser is directly attached to the electrometer, as shown in fig. 137: *a* the insulated plate; *b* the moveable plate in communication with the ground.

The general phenomena of induction already explained are also illustrated by this form of apparatus; and it will now be evident that what is termed electrical *repulsion* depends upon induction to surrounding bodies, as in the case of the gold leaves of the electrometer, or of two similarly electrified pith-balls, which cannot induce towards each other, but do so in all other directions through the molecules of the surrounding medium or dielectric. In the condenser above described, when the plates are near each other so as only to be separated by a very thin stratum of air, induction chiefly takes place from *a* to *b*; but on removing *b* to a distance, the induction of the gold leaves to the nearer surrounding objects becomes manifest, and they appear to repel each other. In these cases, more or less of the inductive force is diverted from one direction into another.



§ 10.—OF NATURAL ELECTRICAL PHENOMENA.

HAVING considered electricity in relation to its most obvious and ordinary effects, we may proceed briefly to examine its influence as a *natural agent*.

Electricity is called into action, upon a grand and sublime scale, in the production of the *thunder-storm*. It has been by no means satisfactorily ascertained to what the electric accumulation, that in such cases ensues, is to be attributed, but it is probably referable to a variety of causes, and connected with some peculiar power in masses of aerial vapour to receive and retain electrical charges, which do not admit of artificial imitation, and cannot, therefore, be satisfactorily explained by experiments upon a smaller scale.

The ancients referred the thunder-storm to the collision and attrition of clouds and vapours, impelled and agitated by currents in the higher regions of the atmosphere; and, in more modern times, before the discoveries in electricity which have been noticed, subtile inflammable and sulphureous exhalations were supposed to exist in the air, and, by their ignition and explosion, to produce the effects.

At an early period of electrical science, an analogy between the electric spark and lightning was suggested. Mr. Grey and Dr. Wall, and afterwards the Abbé Nollet, (*Leçons de Physique Expérimentale*, t. iv. p. 314, Paris, 1748), hinted more explicitly at this analogy. "If any one," says he, "should take upon him to prove, from a well-connected comparison of phenomena, that thunder is, in the hands of Nature, what electricity is in ours; that the wonders we now exhibit at pleasure are small imitations of those great effects which alarm us, and that the whole depends upon the same kind of mechanism; should it be shown that a cloud, formed by the action of the winds, by heat, and by a mixture of various exhalations, is, when opposite to a terrestrial object, as an electrified body when at a certain distance from one that is not electrified, I confess, such an idea, if well supported, would afford me infinite pleasure, and, that it may be supported by many plausible arguments, is obvious to any one well versed in the history of electrical phenomena. The universality of the electric matter, the rapidity of its action, its heat, and its activity in inflaming other bodies; its property of striking them externally and internally, even to their smallest parts; the remarkable instance we have of this effect in the Leyden experiment; the notion which may be legitimately adopted of the effects that might be supposed to arise from a much greater accumulation of electric power: these, and many other points of analogy which I have for some time meditated upon, almost induce me to believe that, in taking electricity as a foundation, one might form much more perfect and plausible hypotheses respecting the origin of thunder and lightning than any that have been hitherto suggested."

Such are the suggestions of Nollet respecting the analogies between electricity and lightning: their truth was afterwards proved by Franklin, who, like his predecessors, meditating upon the similarity of their effects, traced out further resemblances, and at length hit upon the happy expedient of sending up a common kite to an electric cloud, and thus experimentally demonstrating their identity. The following are the particulars of this curious discovery. (*Encyclop. Brit.* Art. ELECTRICITY.)

Franklin begins his account of the similarity of the electric fluid and lightning, by cautioning his readers not to be staggered at the great difference of effects in point of degree, since from that no fair argument could be drawn of the actual disparity of their nature. It is, he says, no wonder that the effects of the one should so far exceed those of the other; for if two gun-barrels electrified will strike at two inches distance, and make a report, at how great a distance 10,000 acres of electric cloud must strike and give its fire, and how loud must be the crash. He then adds, that flashes of lightning are generally crooked and waving, and so is a long electric spark; that lightning, like common electricity, strikes the highest and most pointed objects in its way, in preference to others, such as hills, trees, towers, spires, masts of ships, points of spears, &c.; that it takes the readiest and best conductor; that it sets fire to inflammable bodies, rends others to pieces, and melts the metals. Lightning, he adds, has often been known to strike people blind, and the same happened to a pigeon which had received a violent shock of electricity; in other cases it has killed animals, and they have also been killed by electricity.

Reasoning on these effects, and having observed that pointed conductors appear to attract electricity, he conceived that pointed rods of iron attached to buildings might draw from clouds their electric matter, without noise or danger, and dissipate it at their termination in the earth: the following is his memorandum upon this subject:—"The electric fluid is attracted by points; we do not know whether this property be in lightning, but since they agree in all particulars in which we can already compare them, it is not improbable that they agree likewise in this. *Let the experiment be made.*"

In the year 1752, while waiting for the erection of a spire in the city of Philadelphia, not imagining that a pointed rod of any moderate height would answer the purpose, it occurred to him, that, by means of a common kite, he might have ready access to the higher regions of the atmosphere. Preparing, therefore, a large silk handkerchief, and two cross sticks to extend it on, he took the opportunity of the first approaching thunder-storm, and went into a field, where there was a shed proper for his purpose. But, fearing the ridicule which might attend an unsuccessful attempt, he communicated his intention to no one but his son, who assisted him in flying the kite. A considerable time elapsed without appearance of success, and a promising cloud passed over the kite with no effect, when, just as he was beginning to despair, he observed some loose threads upon the string of the kite begin to diverge and stand erect; on this, he fastened a key to the string, and on presenting his knuckle to it, was gratified by the first electric spark that had thus been drawn from the clouds; others succeeded; and when the string had become wet by the falling rain, a copious stream of electric fire passed from the conductor to his hand. What were Franklin's emotions upon this occasion, it is easy to conceive: we are told that when he saw the fibres of the string diverge, and the spark pass, "he uttered a deep sigh, and wished that the moment were his last;" he felt that his name would be immortalized by the discovery.

Franklin pursued these experiments with much assiduity and success: he erected an insulated iron rod to conduct the electricity of the clouds into his house, and performed with it nearly all the experiments for which he had before employed the common machine; and that no opportunity might be lost of making such experiments, he attached a chime of bells to the electric rod, which gave him notice, by their ringing, of the electric state of his apparatus.

Two French gentlemen, Messrs. Dalibard and Delor, probably were the first who experimentally verified Franklin's hypothesis. The former prepared his apparatus at Marly, near Paris; the latter at his house, which stood upon high ground in that city. Dalibard's apparatus consisted of an iron rod forty feet long, the lower end of which was brought into a sentry-box; on the outside it was fastened to three wooden posts by silken strings defended from the rain. This machine was the first that happened to be favoured by a visit from the ethereal fire. Dalibard himself was from home, but in his absence had intrusted the care of his apparatus to a person of the name of Coisier, on whose courage and industry he could depend: this person, having had all necessary instructions, was directed to call some of his neighbours, particularly the

curate of the parish, whenever there should be any appearance of a thunder-storm; at length the event arrived, and on Wednesday, the 10th of May, 1752, between two and three in the afternoon, Coisier heard a loud clap of thunder; he immediately ran to the sentry-box, and, in the presence of the curate and several neighbours, drew sparks from the conductor. A few days afterwards a successful repetition of the experiment was made by M. Delor at Paris.

These important and interesting experiments were of course repeated in almost every civilized country with variable success: in France a grand result was obtained by M. de Romas. (*Mém. des Sçavans Etrangers*, t. ii.) He had constructed a kite seven feet high, and three wide, which was raised to the height of 550 feet by a string with a fine wire interwoven through its whole length, to render it a better conductor. On the 26th of August, 1756, streams of light were darted from the string of this kite, of an inch in diameter, and ten feet long.

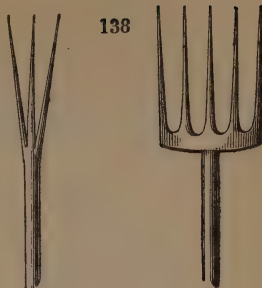
Considering the facility, and, at the same time, the danger of these experiments, it is curious that they have only in one instance been attended by a fatal result, namely, in the case of Professor Richman of Petersburg. He had constructed an apparatus for experiments on atmospheric electricity, which was entirely insulated, and with no contrivance for discharging it when too strongly electrified. On the 6th of August, 1753, he was examining the electricity of this apparatus in company with a friend, and whilst attending to an experiment, his head accidentally approached the insulated rod, and a flash immediately passed from it, through his body, and deprived him of life. A red spot was produced upon his forehead, his shoe was burst open, and a part of his waistcoat singed; his companion was for some time rendered senseless; the door of the room was split and torn off its hinges.

The discovery of the identity of lightning and electricity has not been without its practical results, among which we may especially enumerate the application of *Conductors* to buildings and ships, by which their safety during a thunder-storm is almost ensured. Franklin's original proposition for the purpose is that generally adopted; it consists in erecting a continuous metallic rod by the side of any building which it is intended to protect; the rod is *pointed* at each end, and extended above the highest part of the building at one extremity, the other penetrating deep into the earth, or in contact with water. In establishing this safeguard no other precautions are necessary than to have the top of the rod well and permanently pointed; and it is better of copper than iron, because the former does not so easily acquire a coating of rust, which, being a non-conductor, might possibly diminish its efficacy: it is sometimes well to subdivide the extremity into three or four points: and it should be secured to the side of the house in its descent, and penetrate so deep in the ground as always to be in free contact with a moist stratum of soil; if it ends in a deep well, so much the better. The diameter of the rod should be such as amply to secure it against being melted by a sudden and copious flash of electricity, for which purpose half an inch is fully sufficient; and if the roof is leaded, a broad strip of lead should connect it with the conductor. When a building is very extensive, it is as well to have a conductor at each end; and where a church-spire is to be protected, all clamps and bars

of metal, of any magnitude, used in its construction, should have a metallic connexion, by a strip of lead or otherwise, with the nearest part of the conducting-rod*. A small building containing very dangerous materials, such, for instance, as a powder-magazine, is perhaps most prudently defended from ignition by lightning, by placing the conductor within a few yards of the building, and elevated several feet above it; for this purpose it may be attached to a mast or signal-post in the vicinity.

Conductors for ships have usually been made moveable, with the intention of occasionally attaching them to the mast during dangerous storms; the consequence has been, that they have generally remained packed up below, and not in their place in the time of danger: they are also commonly made of chain, which is improper. Mr. Harris recommends fixed conductors, and has experimentally demonstrated their safety and value.

Persons not otherwise nervous or timid, often experience particular sensations of alarm and discomfort upon the approach of a thunder-storm, arising from some constitutional peculiarity, which perhaps renders them especially sensible of the influence of electricity upon the system. These and others are often led to inquire after the best means of safety upon such an occasion; the directions to be given are few and simple. If out of doors, trees should be avoided; and if, from the rapidity with which the explosion follows the flash, it should be evident that the electric clouds are near at hand, a recumbent posture upon the ground is the most secure. It is seldom dangerous to take shelter under sheds, carts, or low buildings, or under the arch of a bridge. The distance of twenty or thirty feet from tall trees, or houses, is rather an eligible situation, for should a discharge take place, such prominent bodies are most likely to receive it, and the less elevated objects in their neighbourhood may therefore escape uninjured. It is also right, during a thunder-storm, to avoid rivers, ponds, and streams of water, for they are good conductors, and the height of a human being when connected with them is likely to determine the course of the discharge. Within doors we are tolerably secure in the middle of a large carpeted room, or when standing upon a doubled hearth-rug. We should avoid the chimney, for the iron of and about the grate, the soot that lines it, and the heated and rarefied air that it contains, may conduct the lightning; upon the same principle, gilt mouldings, bell-wires, and extensive metallic surfaces of any description, are also in danger of being struck. In bed we are comparatively safe, for feathers and blankets are bad conductors, and we are consequently, to a certain extent, *insulated* in such situation. The cellar has been sometimes recommended as a particularly safe place of resort, and so it



* It not unfrequently happens that the iron or leaden water-pipes attached to houses act as excellent conductors, and supersede the necessity of any specific arrangement.

often is; but sometimes the basement story of a house is that which principally suffers: of this the cause is not very evident*.

We are often told that there is no danger if a certain interval of time can be counted between the flash and the report of the thunder; this is true enough; indeed, if we can count at all, we are safe. Where persons have been killed by lightning, it has generally come upon them so suddenly as to leave no time for precaution; though it must also be admitted that some have suffered from foolishly ridiculing the idea of danger, and wantonly exposing themselves to the storm, walking out to admire its grandeur, or insisting upon opening the windows to look out and observe it, or standing under a tree for shelter. A severe thunder-storm is always an awful and dangerous phenomenon; and while, on the one hand, it is the extreme of folly to neglect common precaution, or to ridicule those that are alarmed, it is, on the other, equally weak to give way to unfounded apprehension.

It is scarcely necessary here to describe a variety of amusing apparatus which has been constructed with a view to show the effects of lightning upon buildings, the means by which it harmlessly traverses good and continuous conductors, and the mischief which it produces when they are insufficient or interrupted. Models of houses, obelisks, powder-magazines, and ships, properly fitted up for these demonstrations, are sold by the philosophical instrument-makers.

The appearance of the heavens during a thunder-storm, the manner in which the clouds assemble, and attract and repel each other, the circumstance of their rising against the wind, and traversing the upper regions of the atmosphere in a variety of contrary directions, are phenomena which it is not difficult to explain by reference to those general laws of electricity which have been already sufficiently explained. Upon the same principles we account for the fringed appearance of a thunder-cloud, and for the ragged excrescences which it projects towards the earth, whilst its upper surface is generally smooth and well-defined. We sometimes observe that a number of such clouds of small dimensions coalesce into a larger one, moving swiftly in all directions, and darting

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* When a tree is struck by lightning, it often happens that it is completely *barked*. This arises from the electricity taking that direction which best conducts it, and which is between the bark and the wood, where there is most sap and moisture. The bark, on such occasions, is often curiously spread round the tree in the form of a circle. When lightning strikes the ground it occasionally indurates and fuses the substances through which it passes. What are termed *sand-tubes* appear to be formed by the passage of lightning through a sandy soil which it fuses in its passage. They are coated with agglutinated sand, and are about the twentieth of an inch thick, very hard, and furrowed upon the exterior. The annexed cut represents one of these tubes, as described by Mr. Irton (*Geol. Trans.*, 1812). In one part of its passage (at *a*) the electric fluid met with a bed of pebbles which were fused into a mass.

flashes from one to the other, whilst the wind rises and often blows in squalls; the lightning is more frequent as the clouds aggregate, and a great expanse of the heavens often appears in an almost continuous blaze of light. The thunder, at first rumbling in the distance, now approaches with various roaring and rattling sounds, and the rain often falls in torrents.

If we watch a severe thunder-storm from the beginning to the end, we observe a singular variety in the appearance of the flashes: the scene is sometimes rendered awfully magnificent by their brilliancy, frequency, and extent, darting sometimes in broad and well-defined lines from cloud to cloud, and sometimes shooting towards the earth: they are often zig-zag and irregular, and sometimes are said to appear as a large and rapidly-moving ball of fire, an appearance usually designated by the uninformed, a *thunder-bolt*, and erroneously supposed to be attended by the fall of a solid body. The report of the thunder is modified, according to a variety of circumstances, depending partly upon the situation of the observer, the nature of the country, and the extent of air which it traverses. Sometimes it sounds like the firing of many muskets at a short distance off; sometimes like the clattering of loose boards upon each other, or the sudden emptying of a large cart-load of paving-stones: in these cases it usually quickly follows the lightning, and is near at hand: when more distant, it rumbles and reverberates, at first with a loud report, gradually dying away and returning at intervals, or roaring like the distant discharge of heavy artillery. In accounting for these phenomena it must be recollected, that the passage of electricity is infinitely rapid; a discharge through a circuit of many miles has been experimentally proved to be instantaneous; the motion of light is similarly rapid, and hence the flash appears momentary, however great the distance through which it passes. But with *sound* the case is very different; it is infinitely slower in its progress, moving only at the rate of about twelve miles in a minute (p. 189). Now supposing the lightning to pass through a space of some miles, the explosion will be first heard from the point of the air agitated nearest to the spectator; it will gradually come from the more distant parts of the course of the electricity; and last of all will be heard from the remote extremity; and the

different degrees of the agitation of the air, and likewise the difference of the distance, will account for the different intensities of the sound, and its apparent reverberations and changes. If the observer be equidistant, or nearly so, from every part of the flash, he will hear a single crash: this will happen if we suppose *a*, (fig. 140), to represent the observer, and *b* the direction of the flash; which is here passing in an uniform line, as it is sometimes observed to do from a small and highly-charged cloud.



The common progress of lightning is, however, much less regular, (fig. 141,) and may be represented by the zig-zag lines *b c*, the spectators



standing at *a*, in which case the sound will first come to them from the nearest point, and will then seem to recede and again to approach, rumbling irregularly as the sound arrives from the different portions of traversed air, some nearer and some further from them, until it is at length lost in the distance. This

irregularity in the passage of the electric discharge is sometimes so considerable, that the thunder is actually lost to the ear at one moment, and heard again at another, and this three or four times successively in the same clap.

There was at one time a controversy among electricians respecting the relative advantages of points and balls in the construction of conductors; but, consistently with Dr. Franklin's original recommendation, points are now universally adopted. Dr. Franklin suggested an experiment in proof of his opinion, which consisted in attaching to the prime conductor of the electrifying-machine one or more large flocks of cotton, so as to resemble electrified clouds. When a point is made to approach these, they collapse and recede, and quickly lose their electricity: when, on the other hand, they are approached by a ball, they are attracted towards it, and the charge is more slowly dissipated.

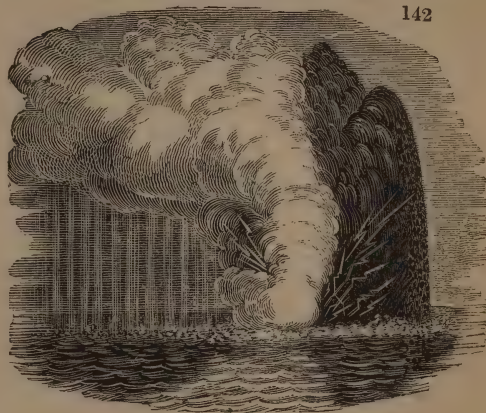
Of the cause of atmospheric electricity we are nearly ignorant: it is true that many changes which are continually going on upon the earth's surface, and in the surrounding atmosphere, are of such a nature as are known to disturb the electric equilibrium; evaporation; change of state or form in the varieties of matter; changes of temperature; chemical action; all these are sources of electrical excitation; but still they can hardly be adduced as offering a satisfactory explanation of the enormous electrical accumulation which a thunder-storm evinces. That sudden, violent, and extensive chemical and mechanical changes in the forms and states of matter, are causes by which electricity is often copiously manifested, is shown by the flashes of lightning that accompany volcanic eruptions, and by the highly electric state of the surrounding atmosphere that attends them.

Another natural phenomenon, which may be referred to electric excitation, is the *waterspout*; it appears to result from the electric attraction of a mass of vapour or cloud acting upon the water beneath: it first causes the appearance of a hillock in the ocean; the water is then drawn up in a column towards the cloud, and the cloud and rain are attracted towards the water.

It occasionally happens that volcanos suddenly break forth in the sea, and sometimes in very deep water; and they are attended by thunder,

lightning, and waterspouts. Of such an eruption a curious account is given by Captain Tillard in the *Philosophical Transactions*, and of its general appearance and effects some notion may be formed from the following wood-cut. In June, 1811, Captain Tillard, on approaching the island of St. Michael, observed several columns of smoke rising in the horizon, which proved to issue from a marine volcano about a mile off the north-west end of the island, whither he proceeded more nearly to inspect the phenomena. "Imagine," he says, "an immense body of smoke rising from the sea, the surface of which was marked by the silver rippling of the waves, occasioned by the slight and steady breezes incidental to those climates in summer. In a quiescent state it had the appearance of a circular cloud, revolving on the water like a horizontal wheel, in various and irregular involutions, expanding itself gradually on the lee side, when suddenly a column of the blackest cinders, ashes, and stones, would shoot up in the form of a spire, rapidly succeeded by others, each acquiring greater

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velocity, and breaking into various branches, resembling a group of pines; these again forming themselves into festoons of white feathery smoke. During these bursts, the most vivid flashes of lightning continually issued from the densest parts of the volcano, and the columns rolled off in large masses of fleecy clouds, gradually expanding themselves before the wind in a direction nearly horizontal, and drawing up a quantity of waterspouts, which formed a striking addition to the scene. In less than an hour a peak was visible, and in three hours from the time of our arrival, the volcano then being four hours old, a crater was formed, twenty feet high, and from four to five hundred feet diameter."

The account then goes on to state, that the eruptions were attended by a noise like the firing of cannon and of musketry intermixed, as also with shocks of earthquakes sufficient to throw down a large part of the cliff on which the observers stood; it is, however, principally to the *lightning* and to the *waterspouts* that I would here direct the reader's attention. Captain Tillard afterwards visited the volcanic island: it was eighty yards high; its crater upon the level of the sea was full of boiling water; it was about a mile in circumference, and composed of porous cinders and masses of stone.

The *Aurora Borealis* is another natural phenomenon, probably connected with or dependent upon electricity; its appearances, indeed, may be, to a certain extent, imitated by artificial electricity, which, when it passes through rarefied air, exhibits a diffused luminous stream, having

much resemblance to the characteristic appearances of the northern lights. "There is," says Mr. Singer, "the same variety of colour and intensity; the same undulating motions, and occasional coruscations; the streams exhibit the same diversity of character, divided at one moment into minute ramifications, and at another beaming forth in one body of light, or passing in distinct broad flashes; and when the rarefaction is considerable, various parts of the stream assume that peculiar glowing colour which occasionally appears in the atmosphere, and is regarded by the uninformed observer with astonishment and fear."

The affections of the magnetic needle and of the electrometer during the appearance of the Aurora, as well as other phenomena connected with it, have been noticed by several eminent philosophers. Halley and Dalton directed the attention of meteorologists to this subject; and, more lately, Captain Franklin has added material information upon it (*Journey to the Shores of the Polar Sea*, Appendix); it has also been accurately described by Captain Parry, who had ample opportunities of observing it in great perfection and splendour, during his perilous voyages in search of a north-west passage from the Atlantic to the Pacific. In this country the Aurora Borealis is rarely seen in perfection. On the 13th of October, 1792, it appeared in great brilliancy; and an account of it, from which the following extract is taken, has been given by Mr. Dalton in his *Meteorological Essays*. The reader may also consult the description given by Mr. Kendall of the Aurora which appeared here in October, 1829 (*Quarterly Journal of Science*).

"Attention was first excited," says Mr. Dalton, "by a remarkably red appearance of the clouds to the south, which afforded sufficient light to read by at eight o'clock in the evening, though there was no moon nor light in the north. From half-past nine to ten there was a large, luminous, horizontal arch to the southward, and several faint concentric arches northward. It was particularly noticed, that all the arches seemed exactly bisected by the plane of the magnetic meridian. At half-past ten o'clock, streamers appeared very low in the south-east, running to and fro from west to east; they increased in number, and began to approach the zenith, apparently with an accelerated velocity; when, all on a sudden, the whole hemisphere was covered with them, and exhibited such an appearance as surpasses all description. The intensity of the light, the prodigious number and volatility of the beams, the grand intermixture of all the prismatic colours in their utmost splendour, variegating the glowing canopy with the most luxuriant and enchanting scenery, afforded an awful, but, at the same time, the most pleasing and sublime spectacle in nature. Every one gazed with astonishment, but the uncommon grandeur of the scene only lasted about one minute; the variety of colours disappeared, and the beams lost their lateral motion, and were converted into the flashing radiations. Notwithstanding the suddenness of the effulgence at the breaking out of the Aurora, there was a remarkable regularity in the manner; apparently a ball of fire ran along from east to west with a velocity so great as to be barely distinguishable from one continued train, which kindled up the several rows of beams, one after another; these rows were situate before each other with the exactest order, so that the lases of each row formed

a circle crossing the magnetic meridian at right angles: and the several circles rose one above another, so that those near the zenith appeared more distant from each other than those near the horizon, a certain indication that the real distances of the rows were nearly the same." This Aurora continued for several hours; there were many meteors, or falling stars, seen at the same time, but they appeared to be below, and unconnected with the Aurora.

During Captain Parry's voyage, he had numerous opportunities of witnessing the Aurora in uncommon magnificence. The following is an abstract of his description of its appearance on the 14th of December, 1821. (*Second Voyage for the Discovery of a North-West Passage*, p. 142). "The Aurora began to show itself as soon as it was dark. Innumerable streams of white and yellowish light occupied the heavens to the southward of the zenith, being much brighter in the south-east, from whence it often seemed to emanate. Some of these streams were in right lines, others crooked, and waving in all sorts of irregular figures, moving with inconceivable rapidity in various directions. Among them might frequently be observed shorter bundles of rays, which, moving even with greater velocity than the rest, have acquired the name of 'merry dancers.' In a short time the Aurora extended itself over the zenith about half way down to the northern horizon, but no further, as if there was something in that quarter of the heavens which it did not dare to approach. About this time, however, some long streamers shot up from the horizon in the north-west, which soon disappeared. While the light extended over part of the northern heavens, there were a number of rays assuming a circular or radiated form near the zenith, and appearing to have a common centre near that point, from which they all diverged. The light of which these were composed appeared to have inconceivably rapid motion in itself, though the form it assumed, and the station it occupied in the heavens, underwent little or no change for perhaps a minute or more. This effect is a common one with the Aurora, and puts one in mind, as far as its motion alone is concerned, of a person holding a long ribbon by one end, and giving it an undulatory motion through its whole length, though its general position remains the same. When the streams or bands were crooked, the convolutions took place indifferently in all directions. The Aurora did not continue long to the north of the zenith, but remained as high as that point for more than an hour; after which, on the moon rising, it became more and more faint, and at half-past eleven was no longer visible.

"The colour of the light was most frequently yellowish-white, sometimes greenish, and once or twice a lilac-tinge was remarked, when several strata appeared as it were to overlay each other by very rapidly meeting, in which case the light was always increased in intensity. The electrometer was tried several times, and two compasses exposed upon the ice during the continuance of this Aurora, but neither was perceptibly affected by it. We listened attentively for any noise which might accompany it, but could hear none, but it was too cold to keep the ears uncovered very long at one time. The intensity of the light was something greater than that of the moon in her quarters. Of its dimming the stars there cannot be a doubt. We remarked it to be in this respect like

drawing a gauze veil over the heavens in that part, the veil being most thick when two of the luminous sheets met and overlapped. The phenomenon had all the appearance of being full as near as many of the clouds commonly seen, but there were none of the latter to compare them with at the time."

My object in the above extracts has been to give an account of those appearances of the Aurora which seem to connect them with electricity, and though Captain Parry neither observed the electrometer nor the magnetic needle to be influenced, Captain Franklin (*Journey to the Shores of the Polar Sea*, App.) remarked them both to be affected. Nairne, Cavallo, and others, have described a peculiar hissing noise as one of the accompaniments of the Aurora; and Dr. Halley, in his description of a remarkable Aurora, (*Phil. Trans.*, vol. xxx.,) ascribes its production to the same influence as that which produces magnetism; and Beccaria conceived the phenomena of magnetism to be dependent upon a circulation of the electric fluid from north to south, originating from several sources in the northern hemisphere.

All *meteors* were at one time considered as derived from electricity; but the showers of stones by which many of them are accompanied show that they must often be ascribed to other sources. What are termed *falling stars* are supposed by some to be of electric origin. These vary a little in size and colour, moving in various directions, but chiefly appearing to shoot towards the earth. They are most common in those states of the atmosphere favourable to electric accumulation, especially on clear frosty nights, or when the sky is cloudless and the wind easterly; in the clear intervals of a showery evening, and on summer nights, when well-defined clouds are floating in a serene atmosphere. They are also common during the prevalence of the Northern Lights, appearing then to be lower than the Aurora; and from their comparative brilliancy, probably moving through a more dense medium.

The appearance of a shooting star may be imitated by discharging a Leyden jar through an imperfectly-exhausted glass tube, or air-pump receiver. The tube should be capped with brass at both ends, and about three feet long and an inch in diameter; if too perfectly exhausted the spark passes in a divided and pale stream of light, but on admitting a little more air it traverses in the form of a bright flash or spark.

It appears from the best-conducted experiments on atmospheric electricity, that in the usual state of the atmosphere it is generally *positive*, but that it frequently changes to *negative* upon the first appearance of rain, snow, or hail. The approach of clouds often influences the electricity of the conductor, so as to produce alternations of the two electricities. There appears, as might be expected, to be a greater accumulation of electricity in the atmosphere during the presence of regular thunder-clouds, than at any other period; a driving fog accompanied by small rain, a fall of snow, and a smart shower on a hot day, are also attended by powerful signs of electric excitation. Hot weather succeeding wet, or wet weather following a series of dry days, are also favourable circumstances for the generation of atmospheric electricity. The atmosphere is least electrical during the prevalence of north-easterly winds, and in that state which produces a disagreeable sensation of dryness and of cold

without a corresponding depression of the thermometer. It has also been remarked, that the usual positive electricity is weakest during the night; that it increases with the sun-rise; decreases toward the middle of the day, and again increases as the sun declines; it then again diminishes and remains feeble during the night; it would, therefore, seem probable that the electricity of the atmosphere is influenced by the same causes that modify the distribution of moisture.

§ 11.—GALVANISM AND VOLTAIC ELECTRICITY.

WE have now acquired such preliminary information upon the subject of electrical excitation, and of the phenomena exhibited by electrified bodies in general, as may enable us to proceed to other cases of the evolution of this singular agent. In the mean time, we may observe, that scarcely any change in the general state of matter is unattended by a disturbance of the electrical equilibrium. Thus, the disruption of solid bodies, changes of temperature, changes of form, are all sources of electricity; breaking up a mass of sugar, tearing asunder the plates of mica, cleaving a piece of dry wood, heating certain minerals, evaporating liquids, and condensing vapours, may be cited as instances; but, of all such changes, those resulting from *chemical* action are apparently the most important, and are immediately connected with those curious cases of the manifestation of electricity, commonly described under the terms *galvanism* and *voltaic electricity*.

In the year 1790, Galvani, of Bologna, discovered that the transmission of a small quantity of electricity through the nerves of a recently killed animal, produced spasmodic convulsions of the muscles: and if the sciatic nerve of a frog be laid bare, and touched with a piece of *zinc*, whilst, at the same time, the muscle is touched with *gold*, similar effects to those of electricity were produced whenever the metals were brought into *contact*, or connected together by *conductors* of electricity: if non-conductors were used to connect the metals, no spasm ensued. Cold-blooded animals retain this kind of excitability longer after death than others, and they are affected by states of electricity so feeble as not to be indicated by the most delicate electrometers. A feeble spark, or the most trivial charge of a Leyden phial, produce analogous effects. These facts soon attracted considerable attention, and were followed up with much diligence and curious results.

Frogs are the most convenient and susceptible animals for these experiments; but when they cannot easily be obtained others may be substituted. The annexed sketch (fig. 143) represents the legs of the frog prepared for galvanic experiments: the skin is removed, and the crural nerves *a a* are then easily found, by gently separating the muscles: *b* is a silver wire passed under both



the nerves, for the convenience of ensuring metallic contact: if the legs be now folded up and placed upon a plate of zinc, convulsions are produced whenever a metallic communication is made between the wire *b* and the zinc plate. A similar experiment may be made with a live flounder, which may generally be procured at the fishmonger's. Place the flounder in a plate upon a slip of zinc, and put a shilling upon its back; then, with a piece of wire connected with the zinc, make occasional contacts upon the shilling, and at each contact strong muscular contractions are produced. According to Dr. Ure (*Dictionary*, Art. GALVANISM), the degree of muscular contraction depends upon the direction of the electric current, and is greater when the zinc touches the nerve, and the copper or silver the muscle, than when this order is reversed*.

In these experiments, if the separate pieces of metal be of the *same* kind, no effects are observed: to produce them, two *different* metals are requisite, and these must be in contact; and those metals which are most difficultly acted upon by acids, opposed to those which are easily soluble, form, in general, the most powerful combination. Thus, gold and platinum produce scarcely any effect; but gold, or platinum, or silver, opposed to iron, tin, or zinc, are very effectual. This part of the subject will, however, be more explicitly inquired into afterwards.

There are many other experiments and illustrations relating to this subject, two or three of which may be here noticed. If a piece of silver be placed *upon* the tongue, and a piece of zinc *under* it, no effect is observed whilst the metals are kept apart; but, if their ends be brought into contact, we immediately perceive a saline taste, and a peculiar sensation, somewhat resembling a very slight electrical shock; sometimes, also, when the surface of the metals is extensive, a flash of light appears to pass before the eyes. This latter effect may be more certainly produced by placing one metal between the upper lip and the gums, and the other upon the tongue, and bringing their ends together as before.

To account for these, and similar effects, Galvani supposed that the nerves and muscles of animals were in opposite electrical states, and that the spasms were produced in consequence of their annihilation by the metallic conductor. But this hypothesis was controverted by Volta, who showed that contractions might be excited by the application of two different metals, but not by one only, and referred the effect to the *electromotive power of the different metals*.

When two dissimilar metals were brought into contact, he found that very feeble electrical states were developed in them. When an insulated plate of zinc was brought into contact with one of silver or copper, the former was found to be in a feebly *positive* state, and the latter

* The phenomena mentioned in the text have given rise to various experiments in reference to the relation between electricity and the vital functions; among these researches, those contained in Dr. Wilson Philip's communications to the Royal Society, and in his *Experimental Inquiry into the Laws of the Vital Functions*, are the most precise. Attempts have also been made, to apply

the stimulus of electricity in cases of suspended animation, from suffocation and drowning. Dr. Ure's interesting account of the effects of galvanism upon the body of a criminal, executed at Glasgow, deserves the attentive perusal of those who are concerned in these medical and physiological applications of electricity; but the subject is too extensive to be entered upon here in detail.

negative, as if a minute portion of electricity had passed *from* the least to the most oxidizable metal. To this transfer, or disturbance of electricity, Volta referred the convulsive motion of the frog's limbs, considering the nervous irritability of the animal as highly susceptible of such influence, and as operating as an extremely sensible electroscope; and the production of similar convulsive twitches by common electric sparks and shocks, was adduced in favour of this opinion.

The following experiment has also been referred to, as a case of electrical excitation, depending upon the *contact* of dissimilar metals:—Place a large plate of metal upon the cap of the gold-leaf electrometer, and sift *zinc* filings upon it through a *copper* sieve, held by a glass handle: the leaves will diverge with *positive* electricity, and the sieve will acquire a *negative* state. Repeat the experiment, substituting a *zinc* sieve and *copper* filings, for the copper sieve and zinc filings, and the divergence of the electrometer will be *negative*, the sieve being *positive*. But when we recollect by what slight causes electricity is sometimes made evident, it becomes a question whether mere *contact* is the only source of its development in these and the preceding cases; whether friction, change of temperature, or even, ultimately, chemical action, may not interfere.

In reference, however, to these cases of supposed electrical excitation by the contact of different metals, it is found that the most oxidizable metal is always *positive*, in relation to the least oxidizable metal, which is *negative*, and the more opposite the metals in these respects, the greater the electrical excitation; and if the metals be placed in the following order, each will become *positive* by the contact of that which precedes it, and *negative*, by the contact of that which follows it; and the greatest effect will result from the contact of the most distant metals. Platinum—Gold—Silver—Mercury—Copper—Iron—Tin—Lead—Zinc—Potassium. Here we have strong presumptive evidence in favour of a chemical cause as the source of electricity, for it is not produced by the most dissimilar *conductors* either of heat or of electricity, but by those which are most opposed in the facility with which they are acted upon by the generality of chemical agents; and it will be moreover found that, upon this chemical action, the direction of the current entirely depends.

Linked as it were with these electrical changes, are certain chemical actions, of which the following are simple instances:—

1. Place a wire of *silver* and one of *zinc* in dilute sulphuric acid, taking care that they do not touch each other; the zinc only will be acted upon by the acid, and the silver remains perfectly inert. Now, bring the upper ends of the wires *into contact*, and the silver will immediately become active: a stream of gas will issue from both wires.

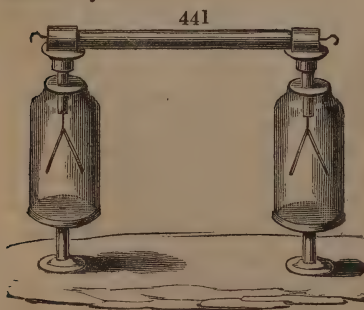
2. Fill a wine-glass with a weak solution of sulphate of copper (*blue vitriol*), and place in it a small plate of clean *iron*, and one of *silver*: the iron will soon acquire a cupreous coating, but the silver remains bright until brought *into contact* of the iron, when it immediately becomes plated with copper.

3. When the *copper* sheathing is affixed to the bottom of ships with *iron* nails, their heads soon corrode and give way, but when the nails are also of copper, no such destructive effect is observed: *iron* railings are

apt to be decayed and dissolved when cemented into stone-work by *lead*; the effect is chiefly observed at the point of junction of the two metals: an *iron* pump put into a *leaden* cistern, or the junction of *iron* and *leaden* pipes, causes the corrosion of both the metals, but first and chiefly of the *iron*: when *copper* is immersed in sea-water it is soon corroded, and gives it a green tint; but if a piece of *iron* or *zinc* be in contact of the copper and the water, no such destruction ensues, the copper being *protected* by the *iron*.

Before we consider these and other *electro-chemical* effects in detail, I shall describe an instrument which will serve to connect them with the phenomena of attraction and repulsion, already adverted to, and to explain the direction of the electric current in these cases of excitation: it is called from its inventor, *De Luc's electric column*. It consists of a number of alternations of two metals, with interposed paper; for this purpose thin paper covered with *silver* leaf may be used, punched out into circular discs of about half an inch diameter, and alternating with similar discs of thin *zinc* foil, so arranged that the same order of succession—namely, *zinc*, *silver*, *paper*, *zinc*, *silver*, *paper*, &c., may be kept up throughout. About five hundred such alternations will be required to produce an active column, and they are most conveniently placed in a suitable glass tube, perfectly clean and dry within, and surmounted at each end with a brass cap, perforated by a screw, by which the plates may be pressed together, and which also serve as the poles of the arrangement; the screw at one end being in contact with the *zinc* plate, and that at the other with *silvered* paper*.

If we hold this column by one of its brass caps, and with the other, touch the cap of the gold-leaf electrometer, a divergence will be communicated to the leaves, which will be found to be *positive* from one end, and *negative* from the other of the arrangement; that end of the column to which the *zinc* surfaces incline, is usually called the *positive* extremity, or pole, and that to which the *silver* plates incline, the *negative* extremity.



If we place the column with each of its extremities in connexion with the electrometers, as represented in the annexed cut (fig. 144), one of the instruments will be *positively*, and the other *negatively* diverged; and on making a direct communication between the two electrometers by a metallic wire, the divergence ceases, but again ensues soon after such communication is broken.

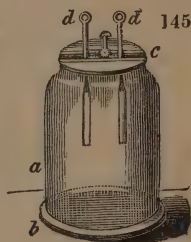
It will be found convenient in experiments with this column to employ two, each containing 500 discs; these may be united end to end,

* Analogous arrangements were made by Hachette and Desormes with pairs of metallic plates, separated by layers of paste mixed with salt; and by Zamboni,

who used discs of paper, gilt or silvered on one side, and covered on the other with a mixture of black oxide of manganese and honey.

so as to form one continuous arrangement. If we examine into the state of the electricity thus excited, we shall find it resembling that of a conductor under induction: that is, there is a positive and a negative pole, and a central point, which exhibits no electricity; upon making a communication between either end of the column and the ground, the electricity of the opposite end becomes proportionally exalted.

In the experiments we are now about to describe it will be found convenient to employ an electrometer, in which each gold leaf is separately insulated, and so arranged as to admit of their being brought nearer to, or carried further from each other. Such an instrument is represented in fig. 145, where *a* is a glass cylinder mounted upon a brass or wooden base, *b*; the cover, *c*, is a thin piece of dry and varnished wood, with a slit in it, in which the glass tubes, *d d*, slide backwards and forwards, and through which, brass wires pass, with a slip of gold leaf attached to each of their lower extremities.



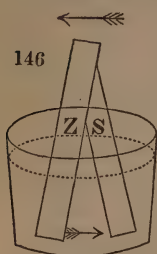
If we now, having duly adjusted the distance between the gold leaves, bring the *zinc* ends of the columns in contact with each of the wires to which they are attached, the leaves *repel* each other; the *silver* ends produce a similar effect: but, if one of the gold leaves be connected with the *zinc* end, and the other with the *silver* end of the column, they *attract* each other; and having thus, by contact, annihilated their opposite electrical states, they separate for a moment, and then again attract and separate as before, a kind of perpetual motion being kept up between the leaves in consequence of the successive electrical charges communicated to them by the column. Upon this principle a variety of instruments have been constructed, under the name of *perpetual motions*: thus, a small clapper may be kept constantly vibrating between two bells; or a light pendulum between two conducting surfaces; and these motions continue as long as the column retains its electric activity, which is often for months or years.

If one end of De Luc's column be connected with the *interior*, and the other with the *exterior* of a Leyden jar, the jar will receive a charge; its knob will affect a gold-leaf electrometer, and on discharging it by a wire, a very small spark will be observed. To obtain this spark, or any luminous appearance, without the intervention of the jar, requires a very extensive series of the metallic alternations.

It will be observed, in regard to this instrument, that its electrical excitement is chiefly that of intensity, and that after its discharge a sensible time intervenes before its power is renewed: its electricity is *apparently* independent of chemical action, and has therefore been considered referable only to the *contact* of the metals. In favour of this opinion it has been urged that whenever any chemical action is apparent in it, its electrical effects cease, as when the zinc or silver become tarnished, or the intervening papers more than ordinarily damp; but it is also rendered inactive by drying the papers so as to deprive them of their hygrometric moisture, and it is said that in the course of years the zinc becomes evidently corroded. It was always presumed that no chemo-

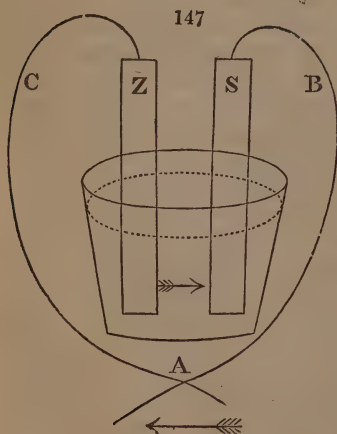
electrical effects could be obtained from these piles, but Mr. Gassiot has succeeded in decomposing iodide of potassium by a column of 10,000 series upon Zamboni's construction. (*Phil. Trans.*, 1839, p. 191.)

What is commonly called "a simple galvanic circle" is formed by partially immersing *two different metals in a dilute acid*, and making a communication between them, either by direct contact, or by some perfect



conductor; one of the metals should be easily, and the other difficultly, or not at all, acted upon by the liquid, and the more opposite the metals are in these respects, the more powerful are the electrical effects observed. In fig. 146, z represents a plate of zinc, and s is one of silver, partly immersed in very dilute sulphuric acid, and in contact at their upper ends; by such arrangement a current of electricity appears to be put in motion, passing from the zinc to the acid, from the acid to the silver, and from the silver again to the zinc, as shown by the

direction of the darts. Or the arrangement may be modified, by immersing the plates separately in the acid, and connecting them by wires, as in fig. 147: the circuit will thus be extended, but the electrical current will be



found moving in the same direction, from the zinc towards the silver, and through the wires from the silver to the zinc, in the direction represented by the arrows. In thus completing the circuit by wires, the electric current may conveniently be transferred through fluid and other bodies, and the circuit may be broken and restored at pleasure, by alternately separating and renewing the contact of the wires at A. It will be observed, that in consequence of the direction of the electric current in this arrangement, the wire B, connected with the silver plate, is conveying electricity to the wire C, united to the zinc plate. Hence B is considered as *positive*, and C as *negative*.

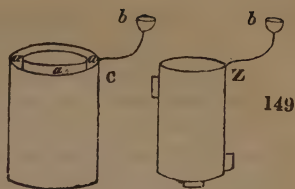
This arrangement may be modified by interposing a few folds of blotting paper, or a piece of flannel dipped in the acid, between the plates, instead of immersing them into the acid itself; or, as in the annexed sectional diagram (fig. 148), the silver or copper plate may itself form the vessel for containing the acid, s representing the wire connected with the cup, and z that with the zinc plate, care being taken that the plate is nowhere in *metallic* contact with the cup.



Another useful modification of this form of apparatus is the following:—c is a cup, composed of two cylinders of sheet-copper, placed one within the other, and closed at bottom, to contain dilute acid: z is a zinc cylinder with a few pieces of cork attached to it, so as to prevent its touching the sides of the cup a, when introduced into its

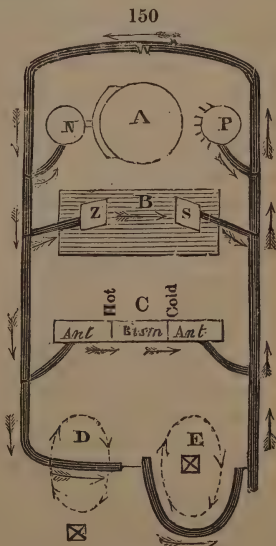
place between them: *b b* are small copper cups, soldered to conducting-wires, and containing a little mercury, for the purpose of conveniently making and breaking the circuit*.

To understand the peculiar phenomena presented by these and similar arrangements, it will be necessary to refer to the important distinctions between electricity of *tension*, accumulated upon surfaces, and manifesting itself by attractions and repulsions, and by discharges passing through air; and electricity in *motion*; the *intensity* of the electricity produced by these simple circles is either null, or so trifling as to require extremely delicate instruments, or electrosopes, to render it sensible; but its quantity is great; and, accordingly, if we make it traverse a very fine metallic wire, placed between the wires *A*, fig. 147, or *z* and *s*, fig. 148, or between the cups *b b*, fig. 149, the wire will become hot, and often ignited; a spark will pass between two fine charcoal points when brought



* It may be well here to allude to the phenomena by which the presence and direction of the electric current are proved. In examining the electricity of the common electrical machine, it has been stated that where the positive and negative conductors are made to communicate by a wire, a current of electricity traverses that wire, and is presumed so to circulate from the positive to the negative side. In the arrangements (figs. 146 and 147) the electricity generated by the action of the dilute acid upon the zinc plate, passes across the liquid to the silver plate, and circulates in the direction of the arrows. In the following diagram the current of the machine is compared with that of the simple galvanic circle. *A* represents the excited cylinder, *N* the rubber, *P* the prime conductor, *w* a metallic wire through which the electric current passes in the direction of the darts; *z* a zinc plate, *s* a silver plate, immersed in dilute acid, and giving rise to a current, the direction of which corresponds with the former. We can now, in either of these arrangements, get evidence of the current, by one or all of the following indications. 1. By heat, as when the metallic circuit, being interrupted, the spark fires ether; or when a very fine platinum wire is interposed between the ends of the thicker wire *A* of fig. 147. 2. By light, as seen in the spark, and the heating of the small wire red hot. 3. By the magnetic properties conferred upon the wires during the passage of the electric current, as shown by the galvanometer,

which will be more fully described afterwards. 4. By the chemical effects of the current when made to traverse certain electrolytes. The further explanation of all these phenomena will be given as we proceed. In this diagram



c represents the direction of the thermo-electric current, *D* that of the marked or north pole of a magnet round the electric current; and *E* that of the electric wire round the magnetic pole; of these also, further explanation will be given in the sequel.

into contact; the *galvanometer* will be powerfully deflected; and certain compound substances, made part of the circuit, will be decomposed: here, then, we have, as evidences of the *current* of electricity above alluded to the production of heat and light, and of magnetic and chemical effects.

There are two circumstances which materially interfere with the *quantity* of electricity put into motion by these arrangements. The one is the *size of the plates*, and the other the *nature and strength of the interposed acid or liquid*; or, in other words, the nature and energy of the *chemical action*. By increasing the superficial extent of the plates, the extent of chemical action is increased, and the *quantity* of electricity proportionately augmented; and in the case of zinc and dilute sulphuric acid, the more rapidly the zinc is oxidized, and the oxide removed, so as to expose successive new surfaces to the agency of the intervening fluid, the greater is the quantity of electricity which traverses the circuit. Indeed, the heating effects of a single pair of plates of great extent of surface is such, that instruments so constructed have been termed *calorimeters*. In an arrangement for this purpose, made under the direction of Mr. Pepys, at the London Institution, (*Phil. Trans.*, 1823,) a sheet of zinc and one of copper were coiled round each other, each being 60 feet long and 2 wide; they were kept asunder by the intervention of hair-ropes, and suspended over a tub of acid, so that by a pulley they could be immersed and removed.

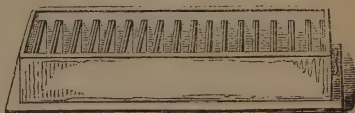
In all these cases, however, the *intensity* of the electricity remains the same, or nearly the same, and, to increase it, we resort to increase of the *number* of the alternations of metals and acid; this constitutes "a compound galvanic circle," and leads to the arrangement originally devised by Volta, and hence termed the *VOLTAIC pile* or *apparatus*. Volta's original pile consisted of a number of plates of two different metals, alternating with moistened flannel or pasteboard, and arranged in regular order of succession. Zinc and copper are the metals in general use: zinc and silver, or zinc and platinum, would furnish a more active series, but the use of the latter metals, in extensive combinations at least, is prohibited by their expense.

To construct the voltaic pile, take from thirty to fifty plates of copper, and as many of zinc, from two to four inches square, and place them in regular order, with an intervening piece of wet flannel of the same size, well soaked in a solution of common salt in water, taking care that the regular succession of *copper, zinc, flannel-copper, zinc, flannel*, is kept up through the series. Having made this arrangement, connect a wire by *perfect metallic contact* with the lowest, or copper, and a similar wire with the uppermost, or zinc plate, having previously slipped a small piece of glass tube upon the wires, to serve as an insulating handle; then, on bringing the upper wire in contact with the condensing electrometer, it will diverge the leaves *positively*, and the lower wire *negatively*, and the same general phenomena will be observed as in De Luc's column. If the fingers be thoroughly moistened, by rubbing them with salt and water, so as in some measure to overcome the non-conducting power of the cuticle, a slight shock will be perceived on touching the extreme wires with each hand: a spark is rarely observed, even in a dark room. But if we now substitute a solution of salt soured by sulphuric acid, for moistening the

intermediate flannel, we shall not observe any material change in the mere electrical power of the pile as indicated by the affections of the electrometer: the shock will be a little more powerful; and a *spark* will be perceived, on bringing the poles together, more especially brilliant when taken between two points of well-burned charcoal attached to the wires from the top and bottom of the pile. Also, if we now bring the wires from the extremities of the pile (which for this purpose should terminate in strips of platinum) near each other, in a glass of acidulated water, gas will be extricated at each conductor.

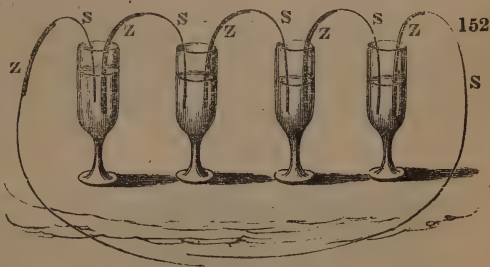
In the construction of the voltaic pile, as just described, much inconvenience results from the method of arrangement, when the plates are very numerous; and the weight of the upper part of the pile presses the moisture out of the lower part, and renders it comparatively inactive. To obviate this, each pair of plates is sometimes soldered together, and cemented in regular order, into a well-seasoned mahogany trough, as in fig. 151; and the intervening cells, which are about a fourth of an inch wide, are filled with water, or other proper liquid, by which the arrangement is rendered active. The apparatus thus constructed is easily filled and emptied, and may be kept clean by rinsing it out with water, after use. A wire, in contact with the last zinc plate, and with the last copper plate, enables us, as before, to complete the circuit.

151

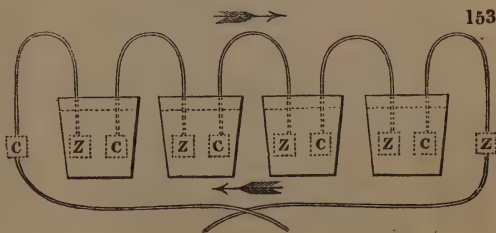


Another form of this apparatus, called by Volta the "*Couronne des tasses*," consists in arranging a row of small glasses or cups, (figs. 152,

153,) containing a very dilute sulphuric acid (or other proper liquid), in each of which is placed a plate or wire of platinum, silver, or copper, and one of zinc, not touching each other, but so connected, that the zinc of the first glass may be in metallic contact or communication with the silver or copper of the second, and the zinc of the second glass with the silver or copper of the third, and so on throughout the series, as shown in the annexed cuts.



152

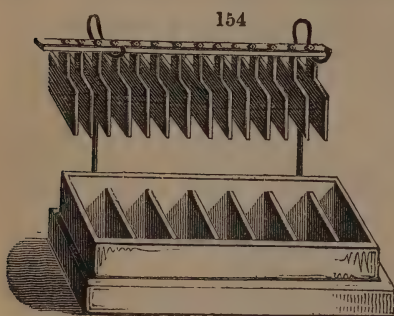


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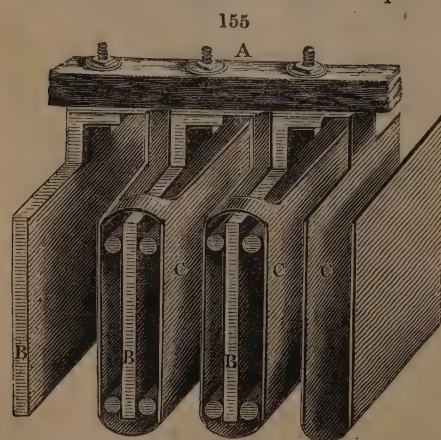
By arrangements of this kind, we can see what happens in each cell of the apparatus; and it will be observed, that when the extreme wires or poles are *in contact*, and a current of electricity therefore passing through the arrangement in the direction of the arrows, each wire or metallic surface immersed in

the liquid is active; whereas, when the connexion between the poles is broken, the silver and the copper cease to evolve gas. In other respects, the general properties of the apparatus thus arranged, resemble those of the other forms above described.

Another good form of the voltaic apparatus is constructed upon similar principles: it consists of a trough of earthenware, with partitions of the same material (fig. 154). The plates, of copper and zinc, are soldered together at one point only, and each united pair of plates is so arranged as to enclose a partition between them; consequently, there is in each cell, a copper plate connected with the zinc of an adjoining cell, and so on, in regular succession; and the connecting piece of the last copper plate is elongated, so as to enable it to dip into the first cell of the next trough, when several such troughs are placed in rows endways to each other; it is there opposed to the ensuing zinc plate of another set, and so on.



The plates are attached to a slip of baked wood, so that the whole may at once be lifted into or out of the cells. This construction, originally suggested by Dr. Babington, has many advantages; it admits the fluid to remain in the trough, while the action of the plates may be suspended at pleasure, by lifting them from the cells; when the plates are corroded or injured, they are also easily replaced. Where many of



these troughs are employed, so as to constitute a powerful battery, it is necessary to be extremely attentive to the regular order of succession throughout the series; if any plates are misplaced, or any single set reversed, a great diminution of effect is the consequence. Much care must also be taken respecting the communications between the troughs, to prevent the accidental displacement of any of the junction-plates. It is well to be provided with a few spare pairs of plates attached to each other by a sufficiently long copper strap, for the purpose of uniting the troughs, where their arrangement requires that they should be placed at angles to each other.

A considerable improvement in the construction of this apparatus was suggested

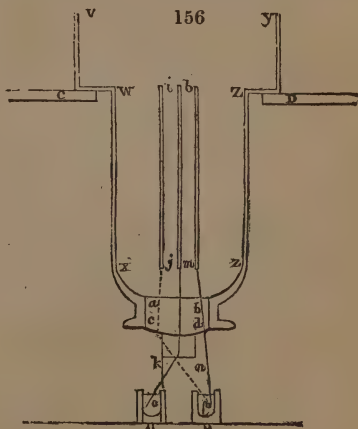
in the year 1815 by Dr. Wollaston. It consists in extending the copper plate, so as to oppose it to both surfaces of the zinc, as shown

in the annexed sketch (fig. 155), where A represents the bar of wood to which the plates are screwed; BB the zinc plates connected as usual with the copper plates c c, which are doubled over the zinc plates, and opposed to them upon all sides, contact of the surfaces being prevented by pieces of wood or cork placed between them, which keep the plates about one-fourth of an inch asunder.

There are many important points of inquiry respecting the phenomena of the voltaic pile, or battery, which cannot be conveniently investigated by any of the preceding arrangements; some of these will be already apparent, and others are connected with effects to which we shall presently advert: to facilitate the experimental examination of such and other questions, Professor Daniell constructed what he termed a *dissected battery*; it is a circular arrangement of ten cells, each provided with a platinum and zinc plate (the latter being amalgamated) and which admit of being combined together in different ways. Over each platinum plate is an inverted and graduated glass tube, filled with the same dilute acid as the cell, in which the hydrogen gas disengaged may be collected and measured.

The following description and figures of this battery are from Mr. DANIELL'S *Introduction to the Study of Chemical Philosophy*, § 726, &c.

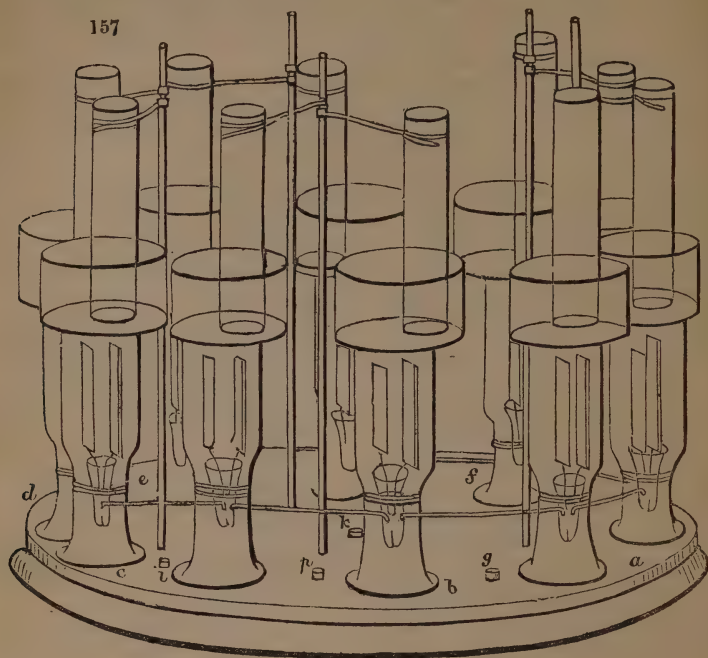
"Fig. 156 represents a single cell of this dissected battery. v w x z z y, is a glass cell resting by its wide rim in a circular hole in the stand c d. i j is a zinc plate, connected by a wire passing through the stopper a b c d, with the mercury cup o, on either side of which is a platinum plate, both of which terminate by wires in the mercury cup, p. Either of these may be used singly by removing the other. The different connexions of the plates with the associated cells may easily be made by wires passing between the mercury cups.



"The whole arrangement of the ten cells with the graduated glass jars is exhibited in the next figure. They are placed upon a stand, a b c d e f, and the connexions between them are easily made and varied by the mercury cups, i p k g," &c.

Mr. Daniell observes, that "however accurately it may be endeavoured to assimilate the cells to each other, it will be found that when connected as single circuits, either singly or together, the action of each will differ; but upon connecting them so as to form a single circular series, the inequalities will disappear, and the amount of gas from each in equal times will be equal. When the cells are combined together in pairs, two adjoining platinum plates being connected, and two corresponding zinc plates, and the five pairs are afterwards arranged in series by wires, leading from each pair of zinc to the next pair of platinum, the irregu-

larity of the action will again disappear. The arrangement is equivalent to a series of five plates of double the standard size, and the amount of force which circulates is determined by the least efficient pair.



“Leaving one pair of cells thus connected, if the others be disunited and recombined with it in single series, the effect will be that of a plate of double size, interposed in a compound circuit with eight single. The gas collected in each of the jars of the double cell will be exactly half of that in the several jars of the single cells; proving that the double plate is reduced in efficiency to the exact standard of the single plates by its combination with them.

“In these arrangements every cell is a generating cell, and adds something to the quantity or intensity of the circulating force; and we see that unequal quantities cannot be generated and circulate in different parts of the same circuit. The effects of various retarding or opposing cells may be strikingly exemplified by the same apparatus. For this purpose the cells may be connected together in single series, substituting in one a platinum plate for the zinc; and the obstacle will be found to react upon the whole series; the action will be found to be reduced by more than one-third, and the quantities of gas collected from each generating cell will be exactly equal to that collected from the retarding cell. Upon repeating the experiment with a similar change in the next cell, the quantity of hydrogen in all the jars will be equal, but reduced to little more than one-tenth, and the current will be apparently stopped by three retarding cells to seven generating cells.”

Mr. Daniell also observes, that "when one of the zinc plates is removed from the regular series, and replaced by a platinum plate which has been previously coated with copper by the influence of hydrogen evolved in a circuit, the phenomena are striking and instructive. No gas will at first be evolved from the coppered plate, but it will oxidate, and the progress of the oxidation may be traced by the gradual blackening of its surface. The oxide, again, will be gradually dissolved, and the bright white surface of the platinum will make its appearance, and oxygen gas will begin to rise from it. At that moment the current will receive a check, which will be appreciable in all the air-jars.

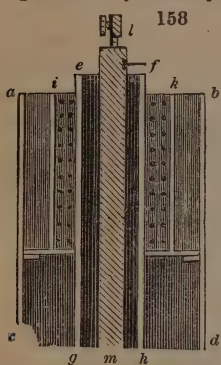
"This mode of measuring the amount of current affinity by its chemical effects, has been applied in the construction of instruments, to which the name of Volta-meter has been given. They consist, in fact, of an independent closed cell, with two platinum plates, from which the gas may be conveniently collected and measured with great accuracy. They may be readily included in any circuit, and, although they check the current in all its parts, they accurately measure the amount which passes through them.

"When a Volta-meter is substituted for one of the ten cells, and the nine have a portion of nitric acid added to their charge, the quantity of hydrogen evolved from their conducting plates is greatly diminished, and becomes irregular; but the quantity of hydrogen indicated by the instrument is nearly treble that of the cells with their original charge.

"By observations made in this manner, it will be soon found that the action of such a compound circuit is not constant; and that it will gradually decline by a quantity which will be quite appreciable at intervals of five minutes. By breaking the connexion for a short period, its energy will be partially recovered, but will again decline as the action is renewed. Upon allowing the charge nearly to exhaust itself, it will be seen that the platinum plates have become incrustated with metallic zinc, originating, doubtless, from the oxide of zinc formed at the generating plates, and reduced by adhering hydrogen at the conducting plates. Its varying quantity and accumulation are amply sufficient to account for the variation and ultimate annihilation of the circulating force; for zinc thus becomes opposed to zinc, and the circuit is destroyed. The momentary breaking of the connexion allows the acid to dissolve off the zinc, which being in contact with the platinum is most favourably disposed for this local action, and upon restoring it, the circulation returns to its first amount, but again speedily declines from the same cause."

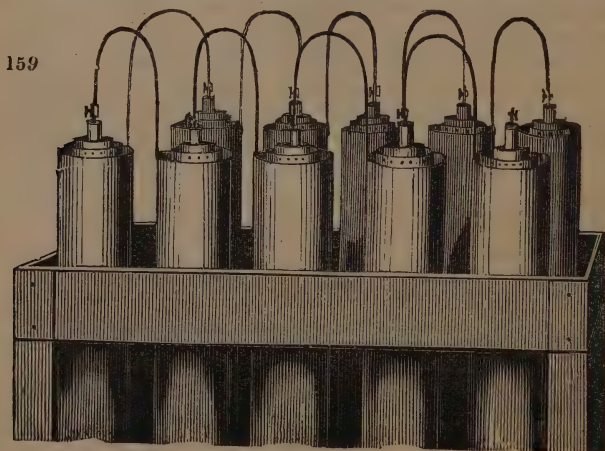
All the forms of voltaic apparatus above described, as well as others which have been devised, are open to the serious objection of inconstancy of action; many causes, some of which are obvious from the description just given of the "*dissected battery*," co-operate to render their power uncertain, and in all it decreases in consequence of the decreasing chemical energy of the interposed liquid upon the generating plate; so that many researches, in which not only the continuous but the equal action of an electrical current during several hours was required, could not be undertaken. This obstacle to the progress of electro-chemical science has been obviated by the invention of the "*constant battery*," contrived also by Professor Daniell (*Phil. Trans.* 1836, p. 117). He describes it

as follows. (*Introd.* § 737). "A cell of this battery consists of a cylinder of copper $3\frac{1}{2}$ inches in diameter, which experience has proved to afford the most advantageous distance between the generating and conducting surfaces, but which may vary in height according to the power which it is wished to obtain. A membranous tube, formed of the gullet of an ox, is hung in the centre by a collar and circular copper plate resting upon a rim placed near the top of the cylinder; and in this is suspended, by a wooden cross bar, a cylindrical rod of amalgamated zinc half an inch in diameter. The cell is charged with a mixture of 8 parts of water and 1 of oil of vitriol which has been saturated with sulphate of copper; and portions of the solid salt are placed upon the upper copper plate, which is perforated like a colander for the purpose of keeping the solution always in a state of saturation. The internal tube is filled with the same acid mixture without the copper. A tube of porous earthenware may be substituted for the membrane with great convenience, but probably with some little loss of power. A number of such cells admit of being connected together very readily into a compound circuit, and will maintain a per-



fectly equal and steady current for many hours together, with a power far beyond that which can be produced by any other arrangement of a similar quantity of the metals.

"One of the cells of the constant battery is represented in the annexed cut (fig. 158). *abcd* is a copper cylinder, in which is placed a smaller cylinder of porous earthenware. Upon the upper part of the copper cylinder rests a perforated colander, *ik*, through which the earthenware cylinder passes. *lm* is a cast rod of amalgamated zinc, resting upon the top of the interior cylinder by a cross piece of wood, and forming the axis of the arrangement. The cell is charged by pouring into the earthenware cylinder water acidulated with one-eighth part of its bulk of oil of vitriol, the space between the earthenware tube and the



copper being filled with the same acidulated water saturated with sulphate of copper; and solid sulphate of copper being placed in the colander."

A number of such cells may be connected into a compound circuit, by wires attached to the copper cylinders, and fastened to the zinc by clamps and screws, as shown in fig. 159.

In the common battery, charged as it usually is with a mixture of sulphuric and nitric acid diluted with water, much local action takes place upon the zinc plates without contributing to the circulating forces, and whilst it is in action the oxide of zinc is reduced by the copper plate. In Mr. Daniell's battery these effects are avoided; the local action is prevented by the amalgamation of the zinc rod, and, upon the copper, nothing but copper can be precipitated*.

The quantity and intensity of the electricity of the voltaic battery depends, as above stated, upon various causes; *quantity* being increased by *extent of surface*, and by *chemical action*, and *intensity*, by *number of alternations*; the best charge for all ordinary purposes consists of a mixture of about 80 or 100 measures of water, two of sulphuric acid, and one of nitric acid. Mr. Faraday's observations on this subject will be found in Series X. of his *Researches*.

The *electro-polar* state of the voltaic battery, that is, the state of its extremities when unconnected, resembles that of De Luc's column, and although the intensity of its electricity is in general feeble, it may be rendered evident by a delicate gold-leaf electrometer, or by the condenser, or by the form of electrometer represented in fig. 145, in which one of the leaves being connected with one extremity, and the other with the opposite extremity of the battery, will become mutually attractive. These effects of *tension*, as belonging to the voltaic pile, are best observed when the alternations are very numerous, the troughs well insulated, the plates perfectly clean, and charged, not with acid, but with water. This I had a good opportunity of witnessing in a large battery of 2000 double plates, constructed, under the direction of Mr Pepys, for the London Institution. When quite new and clean, it was insulated upon wine-bottles, and charged with river-water; it gave a shock resembling that of a Leyden phial, and required some time to recharge itself; the sparks were feeble, but it was permanently active upon the electrometer, and a pith-ball attached by a thread to its positive pole was attracted, at some distance, by another attached to its negative pole; it also communicated a charge to a Leyden battery, when the wires from its extremities were respectively connected with the inner and outer surfaces of the jars. But with all this

* Among the numerous modifications of the voltaic battery lately suggested, there are several which deserve the attention of the practical chemist, especially those of Mr. Smee (*Phil. Mag.*, April, 1840), and Mr. Grove (*Phil. Mag.*, October, 1839). In Mr. Smee's arrangement, silver, or plated copper covered by a film of galvanically precipitated platinum, is used as the negative element, the general construction and intervening liquid being the same as in Wollaston's battery. In Mr. Grove's battery the generating metal is zinc acted on by dilute sulphuric acid; the other element is platinum in nitric acid. These are arranged as in Daniell's constant battery, the inner cells being of porous earthenware. Plumbago, and some of the dense forms of coke, have also been successfully employed as the negative element of the battery.

manifestation of intensity, the energies depending upon *quantity* were very feeble.

It will be observed, that in respect to De Luc's column as well as to the voltaic battery, where single pairs of plates are frequently repeated, the terms *positive* and *negative*, as applied to the zinc and copper or silver ends, are apparently the *reverse* of those applied to the simple circle. The actual direction of the electric current is the same in both cases, but in the simple circle the conducting wire communicates directly with the plate in contact with the fluid part of the apparatus, while in the compound circle it is connected, not with the plate necessarily immersed, but with that associated with it, and therefore of a different kind. The *compound circle*, reduced to its condition of greatest simplicity, would be represented by the following series, consisting of five parts, namely:

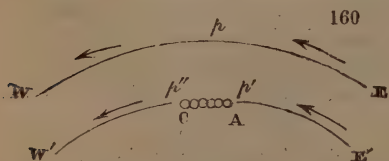
copper—zinc—fluid—copper—zinc.

In this arrangement the copper end is negative, and the zinc end positive. By merely removing the two terminal plates, which in fact are no way concerned in the effect, we bring it to the state of the simple circle, consisting of

zinc—fluid—copper,

in which we find the zinc end negative and the copper positive; this will be evident by inspecting figs. 152 and 153.

The termination of the conductors or wires, connected with the opposite ends of the voltaic battery, are commonly termed its positive and negative *poles*, a term which becomes objectionable when we ascribe to them certain attractive and repulsive powers, and other effects which are the result, not of forces residing in the *poles*, but of the passage or current of electricity; the *poles*, as they are usually termed, are merely the surfaces by which the electricity comes in and goes out; they act simply as a *path* or door to the electric current: in place of the term *pole*, therefore, Mr. Faraday uses *electrode* (from $\eta\lambda\epsilon\kappa\tau\rho\nu$ and $\omicron\delta\omicron\varsigma$ a way), meaning thereby that substance or surface, whether of air, water, or metal, which bounds the extent of the decomposing matter, or electrolyte, in the direction of the electric current. The place at which the electricity enters the electrolyte, he terms the *anode*, that at which it leaves it, *cathode*, in reference,

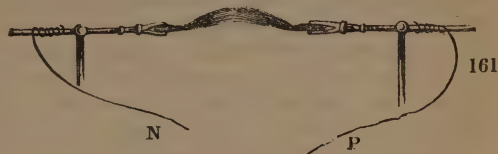


if we suppose the current of electricity to follow the passage of the sun, (that is, to pass from east to west,) in its rising and setting. If, for instance, we suppose a current of electricity traversing a wire in the direction of the darts

in the annexed diagram, and entering at E, then, on separating the wire at p, p' p' would become its *poles* or *electrodes*; and p' would be the positive, or emitting electrode, or the *anelectrode*; and p'' the negative or receiving electrode, or the *cathelectrode*. E being the wire which (in common language) is connected with the zinc end, and w' that connected with the copper end of the battery. Such, therefore, is the meaning which must be attached to the term *poles*. And, supposing the chain of circles $c A$ to represent the *electrolyte*, A would be its *anode*, and c its *cathode*.

Mr. Daniell uses the terms *zincode* and *platinode* instead of positive pole and negative pole, or anelectrode and cathelectrode.

When a powerful voltaic battery is in good action, the following effects are perceived. On making the communication between its extremities by charcoal points, a vivid light and intense heat are produced; and, on slowly withdrawing the points from each other, a constant current of electricity passes between them, producing an arc of light of such intensity as scarcely to



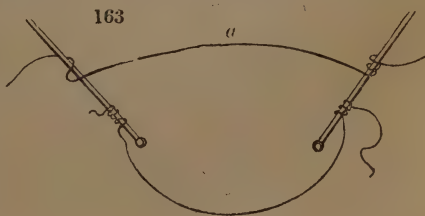
be borne by the unprotected eye, and of the form represented by figure 161. When the charcoal points are gradually withdrawn from each other in a vessel exhausted of the greater portion of its air, as in the apparatus represented by figure 162, the effect is even more brilliant.

The extreme intensity of the *heat*, in this arc of flame, is rendered evident by exposing in it very difficultly fusible substances, which readily melt: even substances infusible by all ordinary methods are thus liquified.

When gold, silver, zinc, or copper leaf are interposed between the poles, they are ignited and burned; and fine wires are heated red or white-hot, according to their lengths and diameters: with an iron wire the combustion is extremely brilliant. All these effects upon good conductors, depending chiefly upon *quantity* of electricity, are most effectively produced by *large plates*. The most formidable battery hitherto constructed is described by Mr. Children. (*Phil. Trans.*, 1815.) The plates were two feet eight inches wide, and six feet high, the copper being opposed to both surfaces of the zinc: these were properly fastened to a beam of wood, suspended by counterpoises from the ceiling of the laboratory, so as to be readily and safely immersed into, or removed from, the cells of acid, which were twenty-one in number, and their united capacities amounted to 945 gallons. A leaden pipe, three-fourths of an inch diameter, was attached to the extreme plate at either end, and immersed into separate basins of mercury, by means of which perfect metallic contact was ensured. The charge consisted of a mixture of nitric and sulphuric acids, with thirty, or occasionally only twenty, parts of water.



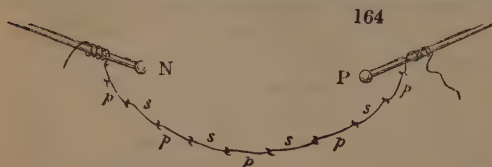
When the poles of this arrangement were united, as shown in figure 163, by a platinum wire eleven-hundredths of an inch diameter, it became red-hot for a length of five feet six inches. In the same way, it ignited eight feet six inches of the same wire of forty-four hundredths of an inch; and a bar of platinum, one-sixth of an inch square,



and two and a quarter long, was not only heated to bright redness, but fused at the end. A number of intractable and very difficultly fusible substances, submitted to the high temperature occasioned by the discharge of this battery through charcoal points, exhibited indications of the most intense heat; but perhaps the most interesting results were obtained by transmitting the electricity through *different* metallic wires. For this purpose either single wires, or two wires of dissimilar metals, were used, of equal diameter and length: one end of each was in contact with one of the basins of mercury communicating with the poles of the battery, and the other end bent to an angle, and the wires connected continuously by hooking them together. The length of each wire was eight inches, and the diameter one-thirtieth of an inch.

Platinum and gold being thus connected, and introduced into the electrical circuit, the platinum was instantly made red-hot, whilst the gold remained unaffected. With a similar arrangement of gold and silver wires, the gold was ignited, the silver not. With gold and copper, both metals were equally heated to redness. With gold and iron, the iron was ignited, the gold not affected. Alternations of platinum and silver three times repeated, all the platinum wires were ignited, but none of the silver.

These experiments, which may be made with a less powerful battery, are extremely beautiful and instructive, especially the last: for this purpose select some fine silver and platinum wire, and cut it into lengths of about two inches; then form a continuous wire by joining these lengths



endways, in alternate order, and suspend it in a festoon between two thick copper wires, forming the poles of the battery, as in fig. 164, having previously tem-

porarily united these poles by a thick copper wire, as is shown at *a* in fig. 163; on removing the latter, the electricity traverses the compound wire, and occasions the ignition of the platinum portions of it only, the silver being unaffected. The object of uniting the poles by a thick copper wire, whilst the compound wire is being attached, is to prevent the sudden fusion of the latter at the point of contact, which often happens when this precaution is not taken.

The cause of these appearances was referred by Mr. Children to the different *conducting powers* of the metals; that platinum conducts electricity less perfectly than silver, and that, consequently, the electric fluid, meeting with greater resistance in its passage through that metal, elicits light and heat; while, on the other hand, passing with comparative facility through the silver, no such effect is there observed. It is obvious that this explanation rests upon the supposition, that resistance to the passage of electricity occasions the development of heat; and as this must be inversely as the conducting power, when any two of the wires, connected continuously, are placed in the circuit, that which is the worst conductor must be most heated; and silver, therefore, which is the best conductor, is not heated red when connected with any other metal.

Mr. Daniell has described (*Phil. Trans.*, 1839, p. 92) the powerful effects of a constant battery of 70 cells. The flame formed a continuous arch of three-fourths of an inch, which striking distance was not increased in vacuo: it was dangerous to the eye, even when protected by coloured glasses, producing, when reflected from an imperfect parabolic mirror in a lantern, inflammation and a scorching like that of the sun: the rays were collected into a focus by a glass lens, and readily burned paper at many feet from their source. The heat was intolerable to the hand when held near the lantern. Paper, steeped in nitrate of silver, was quickly discoloured in the light. The transfer of charcoal from the positive to the negative electrode, produced a cavity in the former and a protuberance upon the latter; and when a platinum rod was substituted for the charcoal forming the negative pole, the transfer from the charcoal at the positive pole still took place, and the metal was coated with carbon, beautifully moulded to its extremity. When this arrangement was reversed, particles of platinum were transferred, and the charcoal on the negative pole became covered with globules of the fused metal. No spark could be made to pass from one electrode to the other, (even when separated by the smallest stratum of air,) previously to the electrodes having been brought into contact; but when two brass balls formed the poles within a very minute distance of each other, and the spark of a small Leyden jar was passed between them, then the battery current was immediately established, and the balls burned*. Mr. Daniell supposes that the Leyden discharge transferred the conducting matter (particles of brass in this case), which was essential to the existence of the voltaic flame, and which was afterwards supplied by its own energy. The arch of flame was attracted and repelled by the poles of a magnet, and it rotated when the flame was drawn from the pole of the magnet itself included in the circuit. The intensity of heat on the side of the positive electrode was much greater than that of the negative. When two stout copper wires of one-fifth of an inch diameter were connected with the extremities of the battery, and held across each other, so that the flame passed between them, the wire at the positive end became red hot, while the other remained comparatively cool. A bar of platinum, one-eighth of an inch square, melted into globules in the former situation, but showed no signs of fusion at the negative electrode. When the positive electrode was formed of the hard carbon taken from a gas retort, and a cavity ground in it, the most infusible metals placed in it were melted in considerable quantities. Rhodium, the native alloy of iridium and osmium, the native ore of platinum, and titanium were thus fused.

The quantity and the intensity of the electricity in the voltaic pile are respectively modified, as has been stated, by the size and number of the plates, and by the action of the intervening liquid. When the zinc plates are perfectly clean, pure water produces certain electrical effects; these are considerably modified by dissolving common salt in it, or employing other saline liquids; but the dilute acids are best calculated

* In reference to the question whether a spark can be obtained before the circuit of the voltaic battery is complete, and also for a description of the brilliant effects of a constant battery of 320 series, see two papers by Mr. Gassiot. *Phil. Trans.*, 1839, p. 183, and *Transactions of the Electrical Society*.

to increase them. If, for instance, we charge three single troughs, each of ten pairs of plates, with water, brine, and very dilute nitric acid, the first will show scarcely any signs of electricity; the second will give a feeble spark and shock; the third will ignite the charcoal points, producing a continuous star of brilliant light. The first will not decompose water; the second does it feebly; the third rapidly. It is obvious, therefore, that with a small number of plates *highly* charged (that is, with dilute acid), we obtain effects equivalent to those of a larger series *feebly* charged; the experimentalist must therefore regulate the strength of the charge according to the number of plates, and the effects which are required. (See FARADAY'S *Researches*, Series X.)

All the effects of *electrical intensity*, such as affecting electrometers, giving shocks, charging jars, decomposing water and saline solutions, and so forth, are, as above remarked, increased by increasing the *number* of the plates, but (*the charge being in both cases the same*) the production of *quantity* of electricity becomes dependent upon the extent of surface of the plates. Thus, if a battery composed of thirty pairs of plates, *two inches square*, be compared with another battery of thirty pairs of *twelve inches square*, scarcely any difference will be perceived in their effects upon *bad* and imperfect conductors; their powers of decomposing water and of giving shocks will be nearly similar; but upon *good* conductors, the effects of the large plates will be very distinct from those of the small ones; the spark, and arc of light between charcoal points, will be much more intense and extensive; and when the charge is transmitted through a fine platinum wire, much of it will be heated red hot; an effect which the small plates are quite inadequate to produce.

The following experiments are adduced by Sir H. Davy, as illustrating these relative effects of *quantity* and *intensity* in the voltaic apparatus:—

Immerse the platinum wires, connected with the extremities of a charged battery composed of *twelve-inch* plates, into water, and it will be found that the evolution of gas is nearly the same as that occasioned by a similar number of *two-inch* plates. Apply the moistened fingers to the wires, and the shock will be the same as if there were no connexion by the water. While the circuit exists through the human body and through the water, let a wire, attached to a thin slip of charcoal, be made to connect the poles of the battery, and the charcoal will become vividly ignited. The water and the animal substance discharge the electricity of a surface probably not superior to their own surface of contact with the metals; the wires and charcoal discharge all the residuary electricity of the plates; and if a similar experiment be made upon plates of an inch square, there will scarcely be any sensation when the hands are made to connect the ends of the battery, a circuit being previously made through water; and no spark when charcoal is made the medium of connexion, imperfect conductors having been previously applied.

In all the preceding arrangements two metals and a fluid are concerned in the evolution of the electric current, and in the case of zinc, acid, and copper, the zinc is termed the generating plate, being that which is oxidized, and the copper the conveying or conducting plate; but, by using certain liquids which act chemically upon the copper and not upon the

zinc, the direction of the current may be inverted, and the copper may become the generator, and the zinc the conductor.

It is, however, by no means essential that two metals should be employed to obtain an electric current; for if only one metal be used, different parts of which are unequally acted on by an acid, or other fluid, electricity will be evolved according to the same law; the portion of the metal most acted on becoming the generator or positive element: thus a current is established when a plate of new and clean zinc and one of oxidized or corroded zinc are used, or when one of the plates is of cast and the other of rolled zinc. Upon the same principle when a strip of copper, clean at one end and corroded at the other, is immersed in dilute nitric acid, an electric current is produced; in all these cases the surface, which is most open to chemical action, corresponds to the zinc, and that least so to the silver or copper of the simple circle above described.

An electric current is also manifested when a single plate of metal of uniform surface is acted upon by two fluids exerting distinct chemical actions upon it. If, for instance, a vessel be half filled with a strong solution of sulphate of copper, and then carefully filled up with dilute sulphuric acid, so that the latter may lie upon but not mix with it, a plate of iron immersed will be so acted on as to produce an electric current, the upper part becoming the equivalent of the zinc, and the lower that of the copper in the simple circle. A plate of copper immersed in the same way will produce a similar effect, and metallic copper in a crystalline form will be deposited upon its lower end. These, and similar phenomena in reference to the source of power in the voltaic pile, have been laboriously investigated by Faraday, in the sixteenth and seventeenth series of his "Experimental Researches in Electricity."—*Phil. Trans.*, 1840.

§ 12.—ELECTROLYSIS.

The *chemical powers*, as they are usually termed, of the voltaic pile were first observed in regard to the decomposition of water and certain saline solutions, by Messrs. Nicholson and Carlisle, in the year 1800, (*Phil. Mag.*, vii., and *Nich. Jour.*, 4to., iv., 183); these were then more accurately investigated in 1803 by Hisinger and Berzelius (*GEHLEN'S Jour.*, i., 115), and, in 1807, Sir H. Davy communicated his celebrated lecture "On some chemical agencies of Electricity" to the Royal Society, in which the electro-chemical powers of the pile were more minutely examined, and which formed the groundwork of the brilliant discoveries to which he was soon afterwards led. There were, however, many important phenomena, more especially those connected with the development of electricity by chemical action, and with the theory of electro-chemical decomposition, which Sir H. Davy, and others, whose researches have enlightened this difficult department of experimental science, either left unexplored, or insufficiently and unsatisfactorily explained: these have lately engaged the attention of Professor Faraday; and his "Experimental Researches in Electricity," published in a succession of papers, communicated to the Royal Society (*Phil. Trans.*, 1832 to 1840), contain the results of his labours, in reference to this branch of knowledge. They have not only, as our preceding pages have shown, explained and enlightened much

that was before unintelligible and obscure in regard to statical electricity, but have also stamped a new character upon electrical as connected with chemical science; in point of originality in devising experiments, skill in carrying them into effect, and perspicuity in tracing out and unravelling the complicated relations and bearings of the new truths which are elicited, he stands, if not unrivalled, at least unsurpassed.

When the electrodes of the voltaic battery are brought near to each other in certain liquids, such, for instance, as *water* and *saline solutions*; or, in other words, when these liquids are made part of the electric circuit, so that the current of electricity passes through them, they are *decomposed*; that is, they yield up their elements in obedience to certain laws; *water*, for instance, is resolved into *oxygen* and *hydrogen*; and the acid and alkaline matter of the neutral salts, which it holds in solution, are separated. In these cases, the elements appear at the poles, or electrodes; not indiscriminately, or indifferently; but the *oxygen* and acids are developed at the *anode*, or surface at which the electricity enters the electrolyte; and the *hydrogen*, and the alkaline bases, at the *cathode*, or surface at which the electric current leaves the body under decomposition.

As the elements of substances thus electrically decomposed are uniformly separated at one or other electrode, it has been assumed that the natural or inherent electricity of such elements is the antagonist of that supposed to belong to the surface at which they appear; in conformity to the law already laid down, "that bodies dissimilarly electrified attract each other;" it has further been assumed, that the elements of compounds are held together by certain electro-chemical forces, more feeble than those belonging to the pile, and that they are consequently overcome by such superior power; that when substances (or their atoms) are similarly electrical they will refuse to combine; and that substances which, in their ordinary states, exhibit no mutual affinities, may be made to enter into combination by communicating to them dissimilar electrical states.

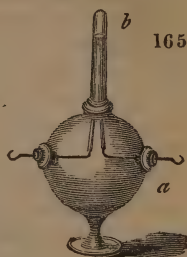
But in classing bodies according to their electrical relations, it is important to state those relations, without involving the expression of hypothetical views, and to this end, Mr. Faraday uses the following terms. All substances susceptible of *direct* decomposition by the electric current, he calls, as already stated, *electrolytes*; *water* therefore is an *electrolyte*; and for the term *electro-chemically decomposed*, he substitutes *electrolysed*. Those elements of the electrolyte which are evolved at the *anode*, he terms *anions*, and those which are evolved at the cathode, *cations*, (*ανιον*, that which goes upwards; *κατιον*, that which goes downwards, in reference to *anode* and *cathode* already defined,) and when these are spoken of together, they are called *ions*: thus, *water* when *electrolysed*, evolves two *ions*, oxygen and hydrogen, the former being an *anion*, the latter a *cation*.

I shall now proceed to a few experimental illustrations of *electrolysis*, or *electro-chemical decomposition*, and afterwards consider the general laws which have been deduced from them*.

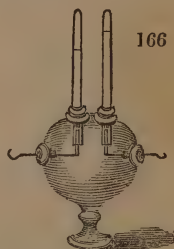
* The terms positive and negative pole are used in speaking of electro-chemical action in two senses: they are fre-

quently employed in reference to certain supposed attractive and repulsive powers belonging to them, and with the same

If two platinum electrodes be brought near each other in water slightly acidulated by sulphuric acid, a stream of gas will issue from each, which in an apparatus similar to fig. 165, may be collected, and examined. *a* is a glass globe with three apertures; two of these (on the sides) are fitted with corks perforated by glass tubes of such length as to approach the centre of the globe, and traversed by platinum wires, which are flattened out into plates at the ends, and turned upwards, within a tenth of an inch of each other. The tube *b* is inverted into the neck of the globe, which it fits loosely, so as to admit of the oozing of a portion of water. This apparatus is then filled with the acidulated water, and the hooked ends of the platinum wires made to communicate with the conducting wires of the voltaic apparatus; gas immediately bubbles up into the tube, and the displaced water trickles out at the neck of the globe. It will be observed, that twice the quantity of gas escapes at the negative pole, or the *cathode* of the water, as compared with that at the positive pole, or at the *anode* of the water: and the tube will be found to contain a mixture of *hydrogen* and *oxygen* gases, in the proportion of *two* volumes of the *former* liberated at the *cathelectrode*, or *negative pole*, and *one* of the *latter* at the *anelectrode* or *positive pole*. If a lighted candle be brought to the mouth of the tube, the mixed gases explode and produce water.



By a simple modification of this arrangement, the evolved gases may be collected in separate tubes; as, for instance, if we employ a globe with two orifices (fig. 166), each having a tube so adapted as separately to receive the gas from each pole. It will then be seen that *two* volumes of *hydrogen* gas, and *one* volume of *oxygen* gas, are respectively collected in the tubes inverted over the *negative* and the *positive* poles. Upon the approach of a taper, the hydrogen gas will burn quietly with a blue lambent flame; and



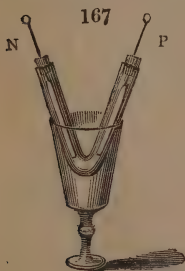
meaning as in speaking of quiescent electricity; but, in reference to electricity in motion, they refer to the surface or passage by which the electricity passes into, and out of the body, under decomposition. In the case, for instance, of a current of electricity traversing a wire or any other substance, and passing from east to west, if we make a break in it, the eastern side of the divided part becomes the positive pole, and the western the negative pole, as may be learned from the diagram fig. 160. But this explanation only applies to the hypothesis of a single electric fluid, traversing the conductor in a given direction: if we assume *two* electric fluids, we must suppose that they traverse the wire con-

necting the poles of the battery in *opposite* directions, in which case, the positive electric fluid must be assumed to issue from the positive pole, and re-enter by the negative; and the negative fluid to issue from the negative pole, and re-enter by the positive. Mr. Daniell calls the positive pole, or the *anelectrode*, the *zincode*; and the negative pole or *cath-electrode*, the *platinode*; the former being the electrode, which in the regular battery would be constructed of zinc, and the latter of platinum. Professor Graham uses the terms *zincous* and *chlorous* poles, the former having the characteristic affinities of zinc, for oxygen, chlorine, &c., the latter those of chlorine, for hydrogen and the metals.

the oxygen may be recognised by immersing into it the glowing wick of a small piece of green taper, which will instantly kindle into flame*.

These experiments are here merely adduced in illustration of the decomposing or electrolytic powers of the current; they show that, under whatever circumstances water is decomposed, the hydrogen is evolved at the cathode, (or at the negative pole,) and the oxygen at the anode, (or positive pole). They are, however, further important, as establishing the composition of water; for, if we reduce the volumes of the gases to their respective *weights*, we shall find that, the volume of hydrogen being = 1, the half volume of oxygen will be = 8, and, consequently, nine parts of water will consist of one part *by weight* of hydrogen, and eight parts *by weight* of oxygen, for the specific gravity of oxygen to hydrogen is as 16 to 1. Hence another verification of the *atomic theory*, in reference to the composition of water and the volumes of its elementary gases (p. 286).

If, instead of pure water, in the experiments just described, we employ *hard* or pump water, we find, that the *saline ingredients*, present in such water, are decomposed, and that their elements are also separated according to certain laws. This may be more strikingly illustrated by dissolving some *salt*, of known composition, in water, and electrising the solution, as in the following experiment. Provide a piece of glass tube, bent at an angle, and placed in a wine-glass, to serve for its foot or support. Fill this syphon with the blue infusion obtained by macerating the leaves of the red cabbage in boiling water, and put into it a few crystals of *sulphate of soda*; then place a strip of platinum foil in each leg of the syphon, taking care that they do not come into contact at the elbow of the tube, and connect one of these with the negative, and the other with the positive, pole of the pile: in a few minutes the blue colour will be changed to *green* in the negative side, and to *red* in the positive side of the tube, indicating



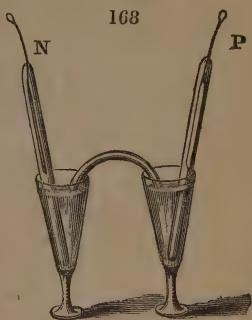
the decomposition of the salt, the alkali or *soda* of which is collected in the *negative*, and the *sulphuric acid* in the *positive*, side. Reverse the poles, and the colours will also gradually be reversed. In this and analogous experiments, it is found that, whenever a neutral salt is decomposed by electricity, the oxide or base is thrown off at the cathode, and the acid at the anode. The bases, therefore, in their electrical relations, rank with hydrogen, and are cathions; and the acids with oxygen, and are anions.

The most insoluble and difficultly decomposable salts may be made to render up their elements in the same way. If, for instance, we substitute for the sulphate of soda in the preceding experiment, a little finely-powdered *sulphate of baryta*, which is insoluble in water, baryta will be

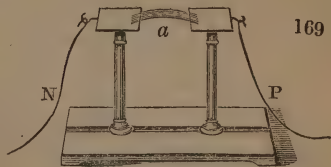
* In these experiments we employ water, to which a small portion of sulphuric acid has been added, and by which its transmitting power in regard to the electric current is much improved; the results are then more rapidly obtained, and by a lower power, but in other respects, not interfered with by the acid.

evolved at the cathode, and there render the liquor green; and sulphuric acid at the anode, rendering it red.

These experiments may be instructively varied as follows:—fill two glasses, connected together by a syphon of large bore, with the blue solution of *sulphate of soda*, and invert in each glass a tube of the same solution, into the upper ends of which platinum wires, terminating in long strips of the same metal, are inserted, as shown in fig. 168; connect these wires with the battery so as to make them the electrodes, and it will presently be remarked that, notwithstanding they are in separate vessels, the blue liquor will, as before, be rendered green and red; and if the experiment be continued for a sufficient length of time, the alkali of the salt will have passed from the side P to N, and the acid from N to P. The acid and alkali appear, in this case, to traverse the connecting syphon in opposite directions; hence the inference that, under the influence of electrical attraction, the usual chemical affinities are suspended.



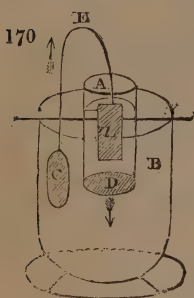
The decomposition of *sulphate of baryta* may be effected in the same way; for this purpose, provide two insulated discs, or very shallow cups of platinum (fig. 169), one of which is to be put into communication with the negative, and the other with the positive, end of the pile; place upon each of these a few grains of finely-powdered (artificial or precipitated) sulphate of baryta, moistened by a drop or two of water, and connect the discs (which should be within half an inch of each other) by some filaments of wet cotton, *a*. In a few minutes *baryta* will be apparent to test-papers at the negative disc, and *sulphuric acid* at the positive.



In some of his experiments on these electrical transferences, Sir H. Davy employed vessels consisting of the substance to be decomposed. Two small cups of sulphate of lime, for instance, were filled with water, and united with moist cotton: they were rendered negative and positive by placing one pole of the pile in each cup; the negative cup soon was found to contain a solution of lime, and the positive cup free sulphuric acid.

If the bent tube, fig. 167, be filled with a dilute solution of sulphate of copper, acetate of lead, or nitrate of silver, the metals will be deposited upon the cathode, and no hydrogen will escape. In this way, M. Becquerel, by employing low voltaic powers, obtained some beautiful results, and succeeded in imitating many crystallized substances found in nature but not previously produced by art. Such experiments have been further extended and improved, and some new and important chemical results obtained from them, by Dr. Golding Bird, (*Phil. Trans.*, 1838): they also have been applied very ingeniously to taking impressions of medals and copper-plates; forming

what have been termed *Electrotypes*, an application originating, I believe, with Professor Jacobi and Mr. Spencer. For this purpose, the following modification of the voltaic arrangement may be used. The piece of metal to be copied, suppose an engraved copper-plate or a medal, or an indented impression of a medal in lead, tin, or fusible metal, is connected by a copper wire with a rod or plate of zinc, the wire being soldered at one end to the zinc, and at the other to the medal or plate to be copied, and of any convenient length: a glass open at both ends is then provided, (a lamp-glass sometimes answers the purpose,) and one end is closed either by plaster of Paris, or by tying over it a piece of bladder: it is then suspended within a larger vessel, filled with a solution of sulphate of copper, which must be kept saturated during the process, either by adding fresh sulphate of copper, or by putting some crystals of that salt into the saturated solution. The smaller vessel is then filled with dilute



sulphuric acid, (1 of acid to 8 of water,) and suspended within the larger one containing the sulphate of copper, as shown in the annexed diagram; where A represents the acid-holder with its porous diaphragm D; B the vessel of solution of sulphate of copper, C the plate upon which the precipitation of copper is intended to take place, and which is connected by the wire E with the zinc plate Z. The darts show the direction of the electric current generated by Z, and transmitted through the diaphragm to C, where the hydrogen of the decomposed water reduces the copper, and gradually precipitates it in

a tough metallic layer. When the deposited copper upon C has acquired sufficient thickness, which will generally be in twenty-four hours, it may be removed by carefully loosening its edge with a knife, and then pulling it gently off the mould. Several moulds may, if requisite be connected with the zinc plate. Some other applications of this process, and directions for its performance, are given in a paper by Mr. E. Solly, in the *Philos. Mag.* for March, 1840.

In some of Sir H. Davy's early experiments on the decomposition of water in glass vessels, a considerable quantity of acid and alkaline matter was elicited, which was traced to the glass: to avoid this source of error, therefore, he electrized distilled water in two vessels of gold, properly connected, thus employing a material which could not furnish impurities to the water: still, however, alkali and acid made their appearance. This evolution of foreign matters, by the electrization of *apparently* pure water, had been observed by others; and their appearance was, by some, referred to a power, supposed to be possessed by electricity, of *generating* the matters evolved; it was even imagined that water might possibly be a simple or elementary body, capable of forming an acid in union with positive electricity, and an alkali with negative electricity. In reviewing these and other opinions, it occurred to Davy, that the water, although carefully distilled, and apparently pure when examined by common tests, might still contain minute portions of foreign matter, rendered evident by the decomposing power of electricity. He accordingly carefully redistilled the water at a low temperature in silver vessels, and on employing

it, thus redistilled, it was found to afford much less indication of impurity; but, even after all precautions, acid and alkali were sparingly evolved. Of this impurity, part was traced to the accidental contact of the hands with the apparatus used, the perspirable matter leaving traces of common salt; and now, aware of this source of contamination, and carefully avoiding it, there were scarcely any traces of acid or alkali to be observed. These extraneous elements, however, notwithstanding all the precautions, were still perceptible after the process of electrical decomposition had been carried on for a length of time; and the only probable source whence they could be derived was the atmosphere, the elements of which, by uniting chemically with those of water, might give rise to the formation of nitric acid and ammonia. This chemical action or combination, Davy thought, might possibly be brought about by electric agency; accordingly, in addition to all the previous precautions, he now conducted the experiments in the exhausted receiver of a good air-pump, and found that, under the careful exclusion of all foreign agents, water was resolved into oxygen and hydrogen only; and, consequently, that there were no grounds for supposing that any new forms of matter were producible by the union of electricity with other bodies.

Another important inference was deduced from the above, and similar experiments; it was obvious that electricity overcame the most powerful chemical attractions; might it not, therefore, when properly applied to different bodies, indicate the existence of substances hitherto unsuspected, and even lead to the knowledge of new elements? Proceeding upon such grounds, Sir H. Davy submitted the fixed alkalis, which were considered at that time as elementary bodies, to the decomposing agency of the pile, and was fortunate enough in this, his first trial, to obtain from them new elements: at the positive pole oxygen was evolved, but brilliant metallic globules appeared at the negative pole, extremely inflammable, and which were shown to be the bases of those bodies. The names *potassium* and *sodium* were given to these new and singular metals; and by analogically applying these phenomena of the decomposition of the alkalis to that of the *earths*, also then on the list of elements, they likewise afforded evidence of decomposition, and, like the alkalis, were shown to be combinations of peculiar metals with oxygen. Many other discoveries have been the result of this new mode of research; but these, as well as the above, will be more fully dwelt upon afterwards.

In all *primary* electro-chemical decompositions, the elements of compounds are evolved with uniform phenomena either at the anode or cathode of the electrolyte, and hence were usually, but incorrectly, stated to be *attracted* to one or other *pole*, and upon the supposition of such attractions, and in reference to that law of electrical action which teaches that bodies *dissimilarly* electrified attract each other, it was assumed that the elements evolved at the anode (or apparently attracted by the positive pole) were inherently *negative*, and those evolved at the cathode (or attracted by the negative pole) inherently *positive*; hence their division into *electro-negative* and *electro-positive* bodies, or, in Faraday's terms, into *anions* and *cations*. In the present state of our chemical knowledge, the *elementary* or *simple bodies* may be regarded as about fifty-five in number: of these, five are usually termed *supporters of com-*

bustion, nine are *non-metallic combustibles*, and the remaining forty-two are *metals*. The five former bodies, when evolved from their combinations by electrolytic action, make their appearance at the anelectrode (zincode, or positive pole); the others are usually observed at the cathelectrode (platinode or negative pole), as are also the metals. But it frequently happens that the evolution of a substance at the electrode is a secondary effect; *sulphur*, for instance, in the decomposition of sulphuric acid, is evolved at the negative pole, not by *direct* electrolysis, but in consequence of the action of the nascent hydrogen; and whenever sulphur is obtained by primary electrolytic action from a compound containing it, it is evolved at the anode, or positive pole; hence, in classifying the elements according to their electrical relations, this distinction must be observed. It is also necessary to guard against the combination of the substance evolved (or *ion*), with the electrode; hence the advantage of platinum electrodes, that metal being acted upon by few of them.

The following table of *simple and compound ions* has been drawn up by Mr. Faraday:—

ANIONS.

Oxygen	Cyanogen	Phosphoric acid	Citric acid
Chlorine	Sulphuric acid	Carbonic acid	Oxalic acid
Iodine	Selenic acid	Boracic acid	Sulphur
Bromine	Nitric acid	Acetic acid	Selenium
Fluorine	Chloric acid	Tartaric acid	Sulphocyanogen.

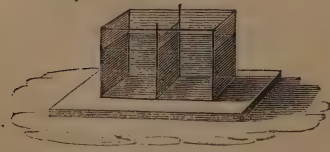
CATIONS.

Hydrogen	Tin	Mercury	Strontia
Potassium	Lead	Silver	Lime
Sodium	Iron	Platinum	Magnesia
Lithium	Copper	Gold	Alumina
Barium	Cadmium	—	Protoxides generally
Strontium	Cerium	Ammonia	Quinia
Calcium	Cobalt	Potassa	Cinchonia
Magnesium	Nickel	Soda	Morphia
Manganese	Antimony	Lithia	Vegeto-alkalis generally
Zinc	Bismuth	Baryta	

Analogy leads us to presume that all simple bodies are *ions*; but this has not yet been experimentally proved in regard to carbon, phosphorus, nitrogen, silicon, boron, and aluminum: several compound bodies, and amongst them alumina and silica, are in the same uncertainty.

The decomposition of water shows the separation of oxygen upon the anelectrode (or positive pole); that of the other, *anions* (or electro-negatives), may be exhibited as follows; and for these, and many other of the experiments of decomposition, the annexed form of apparatus, fig. 171,

171



will be found useful. It is a cell of plate-glass, made by cementing five pieces together with transparent varnish, and supporting them upon a wooden foot, into which they are fastened. The cell is about five or six inches

long, and about an inch broad, and may be divided into two parts, by the insertion of the temporary diaphragm *a*, which is a small frame of cane

with muslin stretched over it. When this is in its place, a separate electrode may be introduced on each side of it: they may most conveniently consist of two pieces of thin platinum, about four inches long and half an inch broad.

To show the evolution of *chlorine* at the anode (or positive pole), fill the glass cell with weak salt and water, acidulated by hydrochloric acid, and coloured blue by the addition of a few drops of a sulphuric solution of indigo; then introduce the electrodes, and in a few minutes the *positive* or *anodic* division will begin to lose colour, and at length become colourless, in consequence of the evolution of chlorine derived from the acid and salt: here, the presence of *chlorine* is rendered evident by its *bleaching power*, which destroys the blue of the indigo.

The presence of uncombined *iodine* is announced by its property of striking a deep blue colour with a solution of starch. To demonstrate its electro-polarity, therefore, fill the cell with a very weak solution of *starch* to which a little common salt and iodide of potassium have been added; then electrize as before, and the *iodine* will show itself at the *anode* (or positive side) by a beautiful *blue* colour.

The presence of *bromine* is announced in the same way by its yellow colour; and of *fluorine* by its action on glass.

The electro-positive bodies, or *cations*, on the other hand, are evolved from their combinations with the anions, at the *cathode* (or negative pole) as is seen in the case of the decomposition of water, &c. There are many striking experiments showing the evolution of the metals at the cathode; and, indeed, whenever solutions of metallic salts are electrolysed, their precipitation at the negative electrode is more or less perfectly observed, according to their facilities of reduction, or deoxidizement*. A plate of silver, for instance, when immersed into a dilute solution of sulphate of copper, occasions no change; but if the silver be made the cathode, (negative electrode,) a precipitation of metallic copper immediately ensues. In the same way solutions of lead, tin, &c., may be decomposed by metals which, under common circumstances, do not effect their decomposition.

When, as in the preceding case, the metals are the cathode, they are at the same time rendered virtually attractive of each other, and of the cations or electro-positive bodies in general: thus, under such circumstances, alkalis, earths, and oxides will be separated upon them; but the same cause which thus renders them apparently attractive of these bodies, renders them as it were repulsive of the anions or electro-negatives, among which are the bodies chiefly characterized by their corrosive and solvent action upon them. A piece of iron, for instance, forming the cathode (rendered *electro-negative*,) will remain bright and clean in water, which, under ordinary circumstances of immersion, would rust and corrode it; but if the iron form the anode (be rendered *electro-positive*,) it then corrodes more rapidly than in plain water; that is, it is

* In the illustrations given in the text, it is to the *results*, that I wish to direct the reader's attention: their *cause*, as I have observed, is frequently a *secondary*, and not a true or *primary*, electrolytic action. There are also many important theoretical considerations arising out of the electrolysis of secondary compounds, more especially affecting our views of the atomic constitution of neutral salts, which will afterwards be noticed. DANIELL, *Phil. Trans.* 1834, p. 97, and 1840, p. 209.

then rendered as it were *attractive* of oxygen, acids, and the other solvent agents, of which, in the opposite case, it is virtually repulsive.

These facts led Davy to infer that certain metallic substances which, under ordinary circumstances, are not acted upon by water and acids, might be rendered *active* by communicating to them the *positively* electrical state; and, on the contrary, that such metals as are easily acted upon by the above-mentioned agents, might be rendered *inert* in regard to them, by giving them the *negatively* electrical state. Silver, for instance, is a metal not acted upon by pure water, nor by salt and water, nor by dilute hydrochloric acid. But, if the electrodes consist of two strips of silver, immersed in water, while the cathelectrode (or negative pole) remains bright, the anelectrode (or positive) becomes discoloured, and a cloud collects about it in the water, which is *oxide of silver*; here, the silver is rendered *attractive* of the oxygen of the water, and combines with it.

If, for water, we substitute a weak solution of common salt, or dilute hydrochloric acid, the *negative* silver will still remain bright, but the *positive* becomes incrustated with a white or gray powder, and is soon corroded; this arises from its being rendered *attractive* of the chlorine contained in the salt and in the acid, and *chloride of silver* is formed.

If we substitute for silver any more oxidizable metal, the effects are still more striking, and we then have a better opportunity of observing the non-action at the negative surface, as opposed to the activity of the positive. For instance, for the silver electrodes substitute two polished plates of *iron*, and immerse them into weak sulphuric or hydrochloric acid, or into a solution of salt—liquids which, under ordinary circumstances, act upon and corrode iron; the negative plate, or cathelectrode, will now remain bright, but the positive, or anelectrode, will be rapidly oxidized and dissolved.

This experiment may be varied and rendered more striking, as follows:—Fill the glass cell, fig. 171, with a weak solution of common salt in distilled water, to which a few drops of a solution of ferrocyanuret of potassium have been added, and immerse one of the iron plates in each partition; the negative side will remain unchanged, but the production of a deep blue colour on the opposite side, will presently announce to the eye the action upon the iron there going on. If we substitute a little infusion or tincture of galls for the ferrocyanuret, the solubility of the iron is then shown by a black tint.

The want of action of the cathelectrode (or negative conductor) shown in these experiments, may be more explicitly illustrated by the following: Silver and copper are readily acted upon by *dilute nitric acid*; it dissolves them with effervescence; but if plunged into the acid when rendered *electro-negative*, (or forming the cathelectrode,) they *resist* its solvent or oxidizing power. It will be borne in mind that, in all these cases of the apparent protection of oxidizable metals in fluids containing water, *hydrogen* is evolved upon the protected surface, whence it either passes off as a gaseous film, or is ready to produce secondary effects by entering into new combinations.

Such cases of the prevention of chemical action may be further illustrated as follows: Dilute some nitric acid with five or six parts of water, so that it may act very moderately upon a piece of *sheet-copper* immersed

into it; in the course of a few minutes the acid will have acquired a slight blue colour from the dissolved copper, which may be rendered more striking by dropping a little of it into a solution of *ammonia*, when a deep blue will immediately announce the presence of copper; but if the copper-plate *be united with one of zinc*, and then plunged into the same acid, it will be found not to have been acted on, the zinc only being dissolved.

Again: immerse a polished plate of iron into a glass of water impregnated with carbonic acid, and in a few hours the water will be discoloured, and a portion of the iron dissolved, as may be shown by the black colour produced on adding infusion of galls. Now, tie a strip of zinc in close contact with the iron, and immerse the two metals into the water: after the lapse of some days, none of the iron will have been taken up; indeed, it will remain as bright as when first put in.

Sir H. Davy aimed at a very important practical application of these facts, as a means of preventing the corrosion of the copper-sheathing of ships. It was generally believed that sea-water had but little action upon pure and well-rolled copper, and that its occasional rapid corrosion depended upon some impurity of the metal, or imperfection in its manufacture. It was found, however, on immersing pieces of the best and purest copper in sea-water, that it soon became covered with a green powder, and was ultimately oxidized and corroded. Davy referred this action to the mutual attraction of the *positive* copper and the *negative* oxygen or acid contained in the water, and, therefore, endeavoured to prevent it by communicating a *negative energy to the copper*, by attaching to it a more oxidable metal, such as zinc, iron, or tin.

In experiments upon the small scale, it was found that a piece of *unprotected* copper, immersed in sea-water, was soon covered by a green powder, part of which was dissolved, and part precipitated; but on attaching to it a piece of zinc, and keeping the metal, thus *protected*, under sea-water, it remained bright and untarnished for several weeks: of the facility, therefore, of thus effectually protecting the copper, there could be no doubt: but a point of great importance in reference to the present question was to determine the relative proportion which it was necessary for the *protecting* metal to bear to the *protected**. When the former was zinc or iron, and amounted to from one-fortieth to one-hundred-and-fiftieth of the copper surface, the latter metal underwent no change or decay; when the zinc was reduced to one two-hundredth, and one four-hundredth, there was some perceptible loss; but it is, to a considerable extent, effectual, where it only amounts to one one-thousandth.

As far, therefore, as *protection* was concerned, the above experiments were satisfactory, and seemed to hold out well-founded hopes of being applicable upon the large scale; but when a negative electric power is thus conferred upon the copper, so as to protect it from oxidizing and corroding agencies, it becomes, (as above explained,) attractive of the cations or electro-positive bodies; among these are the *earthy substances* contained in sea-water, such as lime, magnesia, and some of their compounds: these, therefore, when the plan was adopted upon a large scale,

* See also, in reference to this subject, the curious inquiries of Professor Daniell respecting the mutual relations of the generating and conducting surfaces in voltaic arrangements.—(*Phil. Trans.* 1838, p. 31.)

and a protected vessel sent to sea, were precipitated or deposited upon the copper. Now it seemed, at first, as if this earthy coating would merely act as an additional preservative of the copper; but, unfortunately, the adventitious crust or surface, thus formed, is most favourable to the adhesion of weeds, and of certain marine animals; and these accordingly attached themselves to it so rapidly, and in such abundance, as to render the bottom extremely foul, and to interfere with, and impede the sailing of the vessel. Theory would lead us to expect, that the zinc or iron might be so exactly proportioned to the surface of the copper, as effectually to protect it, without at the same time communicating to it that tendency to attract an earthy crust, which has just been mentioned; but in practice this has been found scarcely attainable*.

It will be obvious, from the preceding details, that electrolytic action tends to the separation both of proximate and ultimate elements; of the separation of the *proximate* elements of compounds, the decomposition of neutral salts furnishes ample instances, in which a compound acid and a compound base are respectively separated at the anode and cathode: whether the sub and super salts or *disalts* and *bisalts* are, or are not, decomposed with precisely the same results, has not, perhaps, been accurately determined, but apparently they are: the case, however, is different with respect to binary compounds of the elementary substances; for among them, (with very few exceptions,) the *proto*compounds, or those consisting of *one atom* or equivalent of an anion, with *one* of a cation, are those only which are directly electrolytic, whilst other binary compounds of the same elements are not so; thus the fused *protochloride*, and *protiodide* of tin are decomposed, but the *perchloride*, and *periodide* are not; these important differences may depend upon conducting power, for no compound which is not, to a greater or less extent, a *conductor*, is susceptible of this decomposition (with the single apparent exception of periodide of mercury, which Mr. Faraday found to insulate whilst solid, but to conduct whilst liquid, and yet was not decomposed).

The cases of *apparent* decomposition opposed to the law just stated are numerous, but they may be referred to *secondary* electrolytic action. When sulphuric acid, for instance, (which is a compound of *one atom* of sulphur, and *three* of oxygen,) is subjected to the action of the electric current, sulphur and hydrogen appear at the cathode, and oxygen at the anode; but as already stated, Faraday has shown that the sulphur is here the result of the action of the *nascent* hydrogen upon the acid, and that in all cases of the true electrolytic decomposition of the sulphurets, the sulphur

* It is to be regretted that the successful applications of scientific reasoning and philosophical discovery to practical purposes, and to the arts of life, are rarely made by their original inventors; and the case before us threatens to turn out an instance of this remark, for a patent has been taken out for covering ships with *iron* plate, protected by zinc; the iron is said to be thus rendered comparatively durable and permanent, and not to have that tendency to become foul, by a little over-protection, which belongs

to copper; whilst its extreme cheapness, in comparison with copper, adds greatly to the value of its application. The galvanic protection of iron by zinc in other cases merits much more attention than it has received; when iron is coated by zinc it is unsusceptible of rust, and in a variety of cases zinc iron is most importantly applicable; but although a "company" was advertised some years ago for the purpose of carrying out this "patented?" discovery, it has never yet been brought into use.

is evolved at the anode, and hence is properly placed in the above table of ions, amongst the anions. He observes, in reference to these cases, that the final result of the action of the electric current upon substances placed between the electrodes, instead of being simple, may be very complicated: that substances may be decomposed either by the direct action of the electric current, or by the action of bodies which that current evolves. There are also two modes by which, in these cases, new compounds may be formed; that is, by the combination of the evolved substances in their nascent states with the matter of the electrode, (of which the formation of oxide of silver, &c., above referred to, is an instance,) or, by their combination with substances, which being contained in or associated with the electrolyte, are necessarily present at the anode and cathode*. This complexity is further increased by the circumstance that such actions may occur simultaneously, and in variable proportions to each other. When the electrolyte is an aqueous solution, or when it contains water, such secondary results are very frequent, but they are not confined to cases where water is present: Becquerel has shown that they are in many instances applicable to the formation of new compounds, and to the imitation of those which are produced by natural operations. (*Ann. de Chim. et Phys.* xxxv. 113.)

Previous to Faraday's researches, it was assumed that all compounds were susceptible of electro-chemical decomposition, and more especially those in which the elements were held together by feeble affinities†; but it is now apparent that conducting power is one essential requisite; and another (probably, at least) a certain atomic relation of the elements to one another; hence a most important application of electrolytic action to the determination of atomic weights. Mr. Faraday has thus expressed this law: "There is but one *electrolyte* composed of the same two elementary ions; hence, only single electro-chemical equivalents of elementary ions, and not multiples, can go to the electrodes." We may infer, therefore, that in the electrolysis of a compound formed of two elementary substances, the elements will be evolved in *single atomic proportions*; hence the inference, that *water* is to be considered as a *primary* atomic combination of single atoms of hydrogen and oxygen: and hence the application of electrolytic action to the determination of the equivalent number of the elements in doubtful cases.

The metallic poles of the voltaic apparatus, or the electrodes, have been spoken of as exerting an attractive power over the elements of the

* The decomposition of a solution of *ammonia*, in which the nascent oxygen of the decomposed water unites to the hydrogen of the ammonia, and sets *nitrogen* at liberty at the anode; and that of *nitric acid*, in which the nascent hydrogen of its water, reacting upon the acid, produces *nitrous acid* at the cathode, are instances of such *secondary* results.

† It follows from Faraday's theory, that the more directly bodies are opposed in chemical affinity, the more easily they are separated by electrolytic action,

provided other circumstances, such as insolubility, deficient conducting power, proportions, &c., do not interfere, "so that in applying the voltaic battery for the purpose of decomposing bodies, not yet resolved into forms of matter simpler than their own, it must be remembered, that success may depend not upon the weakness, or failure upon the strength of the affinity by which the elements sought for are held together, but contrariwise."

electrolyte, but this is not the case, and the common expression, "that certain substances are *attracted* by the negative pole, and others by the positive pole," is so far incorrect, for no *single* elementary substance, or *ion*, has any tendency to pass to either of them; sulphur, for instance, charcoal, or finely-divided metals diffused through water, are indifferent to the transfer or passage of the electricity. The *poles* or *electrodes* may even be *water* or *air*. Thus, if pure water be carefully poured upon a solution of sulphate of magnesia, the platinum conductors may be so introduced and arranged, as to make the saline solution, the anelectrode (positive), and the water, the cathelectrode (negative); in this case magnesia will be deposited *at the line of contact between the water and the solution*, but none of it will pass across the water to the platinum cathelectrode; and in all cases, in which substances have been supposed to travel by mere attraction, a line of compound particles has extended from pole to pole.

It seems proved by Mr. Faraday's experiments, that electricity of very feeble tension may sometimes pass through an electrolyte without effecting its decomposition, and that, in such cases, the decomposition ensues when the conducting power of the electrolyte is improved, or the intensity of the electricity increased. If, for instance, a solution of sulphate of soda be made part of a circuit transmitting electricity of very low intensity, the galvanometer in such a circuit will be deflected, so as to demonstrate the passage of electricity, but no appreciable decomposition of the salt will ensue; on increasing the *intensity* of the current, the deflection of the magnetic needle is not increased, but the acid and alkali of the salt are separated.

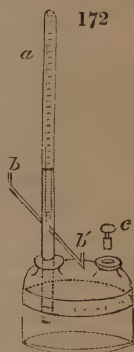
Electrolytes differ in the facility with which they yield up their elements to the influence of the electric current, or in the resistance which they offer to electro-chemical decomposition. (Faraday, *Phil. Trans.*, 1834, p. 448.) The following bodies are electrolytic in the order in which they are placed, those which are first, being decomposed by the current of lowest intensity:—

- Iodide of potassium (solution)
- Chloride of silver (fused)
- Protochloride of tin (fused)
- Chloride of lead (fused)
- Iodide of lead (fused)
- Hydrochloric acid (solution)
- Water acidulated by sulphuric acid.

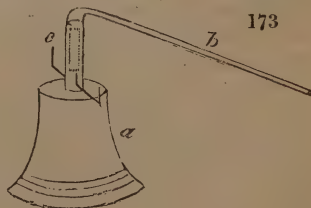
That the chemical power is in direct proportion to the absolute quantity of electricity which passes, was an inference drawn by Mr. Faraday at an early period of his researches, (*Phil. Trans.*, 1833, p. 53,) and afterwards ably demonstrated by a series of conclusive experiments, (*Phil. Trans.*, 1834, p. 102,) which have led to the development of the *definite nature of electro-chemical decomposition*.

Analysis teaches that *water* is composed of 1 part by weight of hydrogen, and 8 of oxygen, and that *oxide of zinc* consists of 32 of zinc, and 8 of oxygen; now suppose a quantity of electricity set free, or in motion, by the oxidizement of 32 parts of zinc by 9 of water, that quantity will also decompose 9 of water by the platinum electrodes,

evolving from it 8 of oxygen and 1 of hydrogen; and the same quantity of electricity transmitted successively through fused chloride of silver, and iodide of lead, so as to decompose them, will evolve 36 of chlorine, and 126 of iodine, at the anodes, and 108 of silver and 104 of lead at the cathodes; these numbers are the exact *chemical equivalents* of the respective elements; accordingly, if we place a portion of *water* anywhere in the electric circuit, the quantity of it which is decomposed, or the quantity of oxygen and hydrogen either separate or mixed, which is evolved, furnishes a *measure*, or mode of expressing the quantity of electricity which has passed in a given interval. Mr. Faraday has constructed several instruments for this purpose, which he terms *Volta-electrometers* or *Voltameters*: among them the two following will be found most useful. *a* (fig. 172) is a straight tube closed at the upper extremity and graduated; through the sides pass the platinum wires *b b'*, being fused into the glass, and connected with two plates within; the tube is fitted by grinding, into one mouth of a double-necked bottle, one-half or two-thirds full of water (acidulated by sulphuric acid to improve its conducting power). The tube is filled by inclining the bottle, and when an electric current is passed through it, the gases evolved collect in the upper part of the tube, and displace the dilute acid, the stopper *c* being left open: when the graduated part of the tube *a* is filled with the mixed gases, the electric circuit may be broken by removing the wires connected with *b b'*, the stopper *c* replaced, and the meter-tube refilled by properly inclining the instrument: a second measure of the gases is then collected, on re-establishing the circuit, and so on.



Another form of the *voltmeter* is the following (fig. 173). It is fixed on a weighted foot *a*, and has the form of a small retort, containing the two electrodes: the neck *b* is narrow and long enough to deliver gas issuing from it into a graduated jar placed in a small pneumatic trough. The electrode chamber, sealed hermetically at the part inserted into the stand, is 5 inches in length, and 0.6 of an inch in diameter; the neck about nine inches in length, and 0.4 of an inch diameter internally.



The chamber *c* is filled up to the neck with dilute sulphuric acid (sp. gr. 1.3). In both these instruments, the contact of the electrodes with each other within the chamber or tube, is prevented by the interposition of pieces of glass-tube.

I must here refer to Mr. Faraday's paper (*Phil. Trans.*, 1834, p. 87, *et seq.*) for some curious and important remarks respecting the influence of different forms of the platinum electrodes in these instruments, and for the experimental proofs, that *variation in the size of the electrodes, causes no variation in the chemical action of a given quantity of electricity upon water*: that their action is uninfluenced by changes in the *intensity*, provided the *quantity of electricity remain the same*: that the quantity

of water decomposed is uninfluenced by the *strength* of the dilute sulphuric acid in the volta-electrometer; that, when other solutions are substituted for the acid, the *constancy of the electrolytic action upon water* is not altered; and that, as before stated, when water, and other electrolytes, are subjected to the influence of the electric current, *the quantity decomposed is exactly proportionate to the quantity of electricity which has passed*, notwithstanding all variations in the conditions and circumstances under which they may at the time be placed.

I shall conclude this part of the subject by the following summary of certain points already adverted to respecting *electrolytes, ions, and electro-chemical equivalents*, taken from Mr. Faraday's seventh series of Experimental Researches in Electricity. (*Phil. Trans.* 1834, p. 111.)

i. A single *ion*, i. e. one not in combination with another, will have no tendency to pass to either of the electrodes, and will be perfectly indifferent to the passing current, unless it be itself a compound of more elementary *ions*, and so subject to actual decomposition. ii. If one *ion* be combined in right proportions with another strongly opposed to it in its ordinary chemical relations, i. e. if an *anion* be combined with a *cation*, then both will travel, the one to the *anode*, the other to the *cathode*, of the decomposing body. iii. If, therefore, an *ion* pass towards one of the electrodes, another *ion* must also be passing simultaneously to the other electrode, although, from secondary action, it may not make its appearance. iv. A body decomposable directly by the electric current, i. e. an *electrolyte*, must consist of two *ions*, and must also render them up during the act of decomposition. v. There is but one *electrolyte* composed of the same two elementary *ions*; at least such appears to be the fact, dependent upon a law, that *only single electro-chemical equivalents of elementary ions can go to the electrodes, and not multiples*. vi. A body not decomposable when alone, as boracic acid, is not directly decomposable by the electric current when in combination. It may act as an *ion*, going wholly to the *anode* or *cathode*, but does not yield up its elements, except occasionally by a secondary action. Perhaps it is superfluous to point out that this proposition has *no relation* to such cases as that of water, which, by the presence of other bodies, is rendered a better conductor of electricity, and *therefore* is more freely decomposed. vii. The nature of the substance of which the electrode is formed, provided it be a conductor, causes no difference in the electro-decomposition, either in kind or degree; but it seriously influences, by secondary action, the state in which the *ions* finally appear. Advantage may be taken of this principle in combining and collecting such *ions* as, if evolved in their free state, would be unmanageable*. viii. A substance which, being used as the electrode, can combine altogether with the *ion* evolved against it, is also an *ion*, and combines in such cases, in the quantity represented by its *electro-chemical*

* It will often happen that the electrodes used may be of such a nature as, with the fluid in which they are immersed, to produce an electric current, either according with or opposing that of the voltaic arrangement used, and in this way, or by direct chemical action, may

sadly disturb the results. Still, in the midst of all these confusing effects, the electric current, which actually passes in any direction through the decomposing body, will produce its own definite electrolytic action.

equivalent. All the experiments agree with this view; and it seems, at present, to result as a necessary consequence. Whether, in the secondary actions that take place, where the *ion* acts, not upon the matter of the electrode, but on that which is around it in the liquid, the same consequence follows, will require more extended investigation to determine.

ix. Compound *ions* are not necessarily composed of electro-chemical equivalents of simple *ions*. For instance, sulphuric acid, boracic acid, phosphoric acid, are *ions*, but not *electrolytes*, i. e. not composed of electro-chemical equivalents of simple *ions*.

x. Electro-chemical equivalents are always consistent; i. e. the same number which represents the equivalent of a substance A when it is separating from a substance B, will also represent A when separating from a third substance C. Thus, 8 is the electro-chemical equivalent of oxygen, whether separating from hydrogen, or tin, or lead; and 104 is the electro-chemical equivalent of lead, whether separating from oxygen, or chlorine, or iodine.

xi. Electro-chemical equivalents coincide, and are the same, with ordinary chemical equivalents.

§ 13.—SOURCE OF VOLTAIC ELECTRICITY, AND THEORY OF THE PILE.

THE electrical equilibrium is so easily disturbed, or, in other words, there are so many causes of electrical excitation, and tending to the production of electrical currents, that it becomes difficult to separate them and to refer to each its due effects: Volta attributed the electricity of the pile to the mere *contact* of the different metals, and regarded the interposed solutions as imperfect conductors, admitting the transfer of electricity when the circuit was completed; and when incomplete, throwing the whole, by induction, into an electro-polar state. This explanation was adopted with some modifications by Sir H. Davy (*Phil. Trans.*, 1807), who seems to have considered the electric state of the pile partly as the consequence of the contact of the opposed metals, and partly of the chemical action of the liquid in the cells; and he concluded, from experiments upon the contact of acids with alkalis and metals, that they became negative and positive in respect to each other*; summing up the whole in the statement, that “Chemical and electrical attractions are produced by the same cause, acting in one case on *particles*, in the other on *masses* of matter, and that the same property, under different modifications, is the cause of all the phenomena exhibited by different voltaic combinations.”—(*Phil. Trans.*, 1826, p. 389.)

Others have referred the electricity of the pile exclusively to chemical action: and Dr. Wollaston not only adopted this opinion (*Phil. Trans.*, 1801), but attributed the activity of the common electrical machine to the oxidizement of the amalgam: this view was opposed by Davy, who, contrary to Dr. Wollaston's experiments, found the electric machine active

* When two metals, or other substances, are brought into contact, and especially when filings of one metal are sifted upon the surface of another, exceedingly feeble *electricity of tension* may be shown by a very delicate electrometer;

but in these cases, and also when solid *acids* and *alkalis* are used, *friction*, change of temperature, and even chemical action, cannot, as already observed, always be avoided.

in atmospheres of hydrogen and of carbonic acid, and in the latter more so than in atmospheric air, probably on account of its greater density.

The phenomena of De Luc's column were considered by some as ample proof of the correctness of the "theory of contact," while others ascribed its electricity to the chemical action of the moisture hygrometrically retained by the paper; but this instrument seems to require more minute and accurate examination before any satisfactory conclusions can be drawn from it*.

That electricity is produced in voltaic arrangements, *independent of contact*, and apparently by *chemical action only*, has been satisfactorily shown by Faraday, for he found that a single pair of plates, so arranged as to avoid metallic contact and every other source of electricity except chemical action, produced a current which not only deflected a galvanometer, but decomposed iodide of potassium. The following was the form of his experiment.—(*Phil. Trans.*, 1834, p. 426.)

A plate of zinc, about eight inches long and half an inch wide, *a* (fig. 174), was cleaned and bent in the middle to a right angle. A plate of platinum, about three inches long and half an inch wide, *b*, was fastened to a platinum wire, and the latter bent as in the figure. These two pieces of metal were arranged together as delineated, but as yet without the vessel *c*, and its contents, which consisted of dilute sulphuric acid mingled with a little nitric acid. At *x* a piece of folded bibulous paper, moistened in a solution of iodide of potassium, was placed on the zinc, and was pressed upon by the end of the platinum wire. When under these circumstances the plates were dipped into the acid of the vessel *c*, there was an immediate effect at *x*, the iodide being decomposed, and iodine appearing at the *anode*, i. e. against the end of the platinum wire. As long as the lower ends of the plates remained in the acid, the electric current continued, and the decomposition proceeded at *x*. On removing the end of the wire from place to place on the paper, the effect was evidently very powerful; and on placing a piece of turmeric paper between the white paper and zinc, both papers being moistened with the solution of iodide of potassium, alkali was evolved at the *cathode* against the zinc, in proportion to the evolution of iodine at the *anode*. Hence the decomposition was perfectly polar, and decidedly dependent upon a current of electricity passing from the zinc through the acid to the platinum in the vessel *c*, and back from the platinum through the iodic solution to the zinc at the paper *x*. That the decomposition at *x* was a true electrolytic action, due to a current determined by the state of things in the vessel *c*, and not dependent upon any mere direct chemical action of the zinc and platinum on the iodide, or even upon any *current* which the solution of iodide might by its action on those metals tend to form at *x*, was shown,

* All the inquiries relating to the source of power in the voltaic pile have lately been submitted to a searching and masterly investigation by Faraday, the details of which (in addition to his former experiments) are contained in the

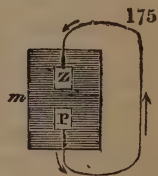
16th and 17th series of his *Experimental Researches*, already quoted. These papers only reached me whilst the present pages were going through the press, or I should have quoted them more in detail.

in the first place, by removing the vessel *c* and its acid from the plates, when all decomposition at *x* ceased, and in the next by connecting the metals, either in or out of the acid, together, when decomposition of the iodide at *x* occurred, but in a *reverse order*; for now alkali appeared against the end of the platinum wire, and the iodine passed to the zinc, the current being the contrary of what it was in the former instance, and produced directly by the difference of action of the solution in the paper on the two metals. The iodine of course combined with the zinc.

So far, therefore, the evidence of the current of electricity *independent of metallic contact* is complete. It is now to be shown how *chemical action* becomes the source of the electricity in the voltaic battery, and for this purpose it will be necessary to trace it from the simple to the compound circle.

In the following illustrations, for which I am indebted to Mr. Faraday, it is supposed that *pure* zinc is used; which, unlike the common zinc* of commerce, is very slowly acted upon by sulphuric acid diluted with six or eight parts of water.

Let *z* (fig. 175) represent a piece of such zinc, and *p* a piece of platinum, both immersed in dilute sulphuric acid; if they do not touch each other, scarcely any action will take place on the zinc, and none on the other metal; but if they touch, or if they are connected by a long wire of zinc or platinum, as represented in the figure, then action takes place; oxygen from the water combines with the zinc, and forms an oxide, which dissolves; and the equivalent of hydrogen is evolved, and appears against the platinum; whilst the connecting wire exhibits all those characters which show that a current of electricity is passing through it. The *direction* of this current is essentially connected with the chemical action on the zinc, and the evolution of hydrogen on the platinum, and may, at any time, be identified by comparing it with the electricity of the common machine. If the prime conductor and rubber of a machine be connected by a wire, the electricity is said, by a conventional expression, to be passing *from* the conductor through the wire *to* the rubber (see fig. 150, A, where *p* represents the conductor, and *n* the rubber); and, admitting that standard of reference, it is found in the experiment just described, that the current of electricity produced is from *p* through the wire to *z*. There are many other solutions, which, if used between the metals *z* and *p*, will cause a similar effect when the latter are connected by the wire, but the current is *always* in the same direction, and it is also always the zinc which enters into combination. Thus a solution of hydriodic acid, or of the iodide of potassium, will cause iodine to combine with the zinc, hydrogen will appear at the platinum, and a current of electricity will exist in the wire, but of weaker power than before.

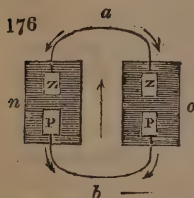


* The impurities in common zinc seem to be the cause of the rapid action exerted upon it by diluted sulphuric acid, which oxidizes it with the evolution of hydrogen. Pure zinc, on the contrary, or, as Mr. Sturgeon has shown, zinc

which is superficially amalgamated with mercury, is not so acted on, and hence the advantage of using it in cases where the *ordinary* and the *voltaic* action require to be separately observed.

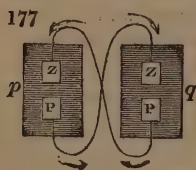
In producing this effect, there are two circumstances which seem to be essential, namely, the immersion of the zinc and platinum in the solution, and the metallic contact of the metals, either directly, or by means of the wire: if the contact be broken the current is stopped, and the action on the zinc ceases; or if the metals be taken out of the solution, the action on the zinc of necessity ceases, and again the current is stopped. Hence it became a question for many years, which, though much argued and experimented upon, has only recently been decided, whether it was the chemical action on the solution, or the contact of the metals, which was the real cause of the electric current, and other concomitant effects.

But now consider fig. 176, and let n and o be two vessels like to m (fig. 175), each containing dilute sulphuric acid and pieces of zinc and platinum, and let the two $z z$ be connected by a zinc wire, and the two $p p$ by a platinum wire: no chemical effects will occur, nor any current of electricity be formed; but the moment a wire of any metal is stretched from a to b , a current of electricity will run up it, dividing right and left, as is shown by the arrows, and oxidation of both zincs will take place, accompanied with the evolution of hydrogen at both platinum.



Consider this cross-wire as still retained in its place, but the dilute sulphuric acid removed from the vessel o , and replaced by a solution of the iodide of potassium. Still the currents will exist, as represented by the arrows; the chemical action will remain unchanged in the vessel n ; and in the vessel o , iodine will combine with the zinc, and hydrogen appear against the platinum. As yet the conditions both of *chemical action* and *metallic contact* exist, the cross-wire from a to b ensuring the latter; but now remove that wire, and instead of a cessation of action, the following change of effects will take place: the electric current from b across to a of course no longer exists; that from a through the vessel n to b will be weakened, and the chemical action in n much diminished; but the current from a through o to b will be actually inverted, and the chemical action in o will be inverted also, and the iodine will now appear in its free state against the platinum p , instead of combining with the zinc, and the hydrogen will appear at the opposite side.

Hence, not only is it proved that metallic contact is not necessary, and that chemical action is the cause of the phenomena, but also that two distant chemical actions may be opposed, and the weaker made to yield to the stronger; and thus, *electro-chemical excitation* and *electro-chemical decomposition* are shown existing together in the simplest manner as *cause* and *effect*.



If two distant chemical actions can be thus shown connected together in *opposition* to each other, so also can they be shown with equal simplicity associated in accordance with each other; and in this consists the *principle of the voltaic pile or trough*: for consider again the tendencies and directions of the two sets of forces, as indicated by the arrows, in the vessels n and o , fig. 176, and then divide the

connecting wires at *a* and *b*, connect the right-hand end of *a* with the left-hand end of *b*, and the right-hand end of *b* with the left-hand end of *a*, as in fig. 177, and then it will be seen by simple inspection, (what is found as a matter of fact,) that the forces in *p* and *q* aid and exalt each other, instead of exerting a mutual opposing action.

Fig. 178 is the representation of three such actions combined, and with 300 or 3000 the principle is the same; the pull on the general current being, as it were, aided by every recurrence of the zinc, and its vigour and intensity exalted.



In reflecting upon the source of electricity in voltaic arrangements, and upon the definite nature of its action, as shown in the experiments above quoted, it becomes almost impossible to doubt the *identity* of the cause of chemical and electrical phenomena, and from an attentive consideration of the manner in which the elements of electrolytes are evolved at the anode and cathode, the insufficiency of that theory which referred the phenomena of their decomposition to the mere *attractive powers of the poles* must be quite obvious: they must certainly be attributed to some specific action of the electric current, pervading the whole of its course through the electrolyte; and if we regard it, with Faraday, (*Phil. Trans.*, 1833, p. 696,) as “an axis of power having contrary forces, exactly equal in amount in contrary directions,” we may also assume that electro-chemical decomposition is produced “by an internal corpuscular action exerted according to the direction of the electric current, and that it is due to a force, either superadded to, or giving direction to the ordinary chemical affinity of the bodies present. The body under decomposition may be considered as a mass of acting particles, all those which are included in the course of the electric current contributing to the final effect; and it is because the ordinary chemical affinity is relieved, weakened, or partly neutralized by the influence of the electric current, in one direction, parallel to the course of the latter, and strengthened or added to in the opposite direction, that the combining particles have a tendency to pass in opposite courses.”

§ 14.—IDENTITY OF VOLTAIC AND COMMON ELECTRICITY.

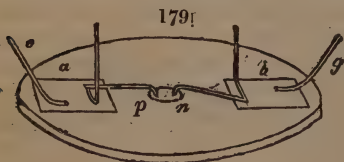
THE phenomena of the voltaic pile are, upon a superficial view, so different from those of common electricity, as frequently to have been referred to a distinct cause, and although they were found, when more accurately compared, to present many analogies, it was long before they were allowed to be absolutely identical. Mr. Faraday was led to revise the experiments already made in reference to this question, and to devise many new illustrations of it: his results are published in the third series of his *Experimental Researches*. (*Phil. Trans.*, 1833, p. 23.) He has arranged electrical phenomena, for the purpose of this comparison, under two heads; namely, those connected with electricity of *tension*, and those connected with electricity of *motion*; the former includes attractions and repulsions at sensible distances: the latter (or the effects of electrical currents) includes the production of heat, magnetism, chemical decomposition, physiological phenomena, and the spark.

1. The *attractions and repulsions* produced by voltaic electricity, and so far identifying it with that of the common electrical machine, have been above described.

The escape of common electricity through rarefied air, is another effect due to its tension. On endeavouring to discharge a voltaic battery of 140 pairs of plates by approximated pointed wires, either with intervening air, or in a vacuum, no indications of a current, either by magnetic or chemical action, were obtained; but upon *heating* the air between the points, by the flame of a spirit-lamp, the current passed, so as to decompose iodide of potassium, and deflect the galvanometer in another part of the circuit. The arc of flame between charcoal points in air and in a vacuum is a similar phenomenon. Another proof of the tension and quantity of the electricity of the pile, is the charge of a Leyden battery, which may be effected by De Luc's column and by the voltaic battery.

2. As concerns *electricity in motion*, that of the voltaic apparatus produces heat, magnetism, chemical decomposition, shocks, and sparks, and in these respects the analogies with common electricity are complete. Of the *heating power* of common electricity, instances have been already given, both as relates to the common spark and to that of the Leyden jar or battery. For delicate experiments upon this subject, Mr. Harris's beautiful and sensible electrometer may be used. (*Phil. Trans.*, 1827, p. 17.) The production of *magnetism* by common electricity has also been satisfactorily proved, by the deflection of the galvanometer*, and by the simple experiment of affixing a steel needle at right angles to a wire through which the Leyden jar or battery is discharged, and which receives permanent magnetism.

The power of common electricity to effect *polar chemical decomposition*, was first shown by Dr. Wollaston (*Phil. Trans.*, 1801, p. 427), and has been amply and excellently verified by Faraday. Upon a glass plate (fig. 179) placed over, but raised above, a piece of white paper, so that shadows may not interfere, put two pieces of tin-



foil *a b*; connect one of them by an insulated wire *c* with the positive conductor of the machine, and the other by the wire *g* with the ground, or with the negative conductor: provide two pieces of fine platinum wire, bent as in fig. 180, so that the part *d f* shall be nearly upright, whilst the whole is resting on the three bearing points *p e f*: place these as in fig. 179; the points *p n* then become the decomposing poles. Place a large drop of *hydrochloric acid*, rendered blue by sulphate of indigo, so that *p* and *n* may be immersed in it at opposite sides, then send a current of electricity through it from a machine in good action, and *chlorine*, shown by its bleaching effects, will be evolved at *p*. This experiment is the counterpart of that with voltaic electricity, described in the first paragraph of page 311. Place a drop of

* By Mr. Colladon of Geneva, and in Faraday's experiments (*Phil. Trans.*, 1833, p. 30).

solution of *iodide of potassium* mixed with starch between the poles, and the current will evolve *iodine* at *p*. Put a drop of solution of *sulphate of copper* between the poles, and the current will then cause the precipitation of *copper* at *n**.

In all these experiments the direct passage of *sparks* must be carefully avoided. If *sparks* are passed over moistened litmus-paper, it is reddened; and if over paper moistened by iodide of potassium, iodine is evolved; but these effects must be carefully distinguished from those due to true *electrolytic* action, and must be cautiously avoided when the latter are sought for. The effect just mentioned is due to the formation of *nitric acid* by the combination of the oxygen and nitrogen of the air: the acid so formed, though very small in quantity, is in a high state of concentration, and therefore reddens the litmus-paper and decomposes the iodide. By moistening a very small slip of litmus-paper in a solution of caustic potassa, and then passing a succession of electric sparks over its length in the air, Mr. Faraday gradually neutralized the alkali and ultimately rendered the paper red, and on drying it he found that *nitrate of potassa* had resulted from the operation, and that the paper had become touch-paper. These experiments furnish simple, beautiful, and ready means of illustrating Cavendish's experiment of the formation of nitric acid from atmospheric air; and render it probable that the singular odour produced by the electric discharge, as when the electricity of a powerful machine is suffered to pass off by points, or in a succession of long and rapid sparks through the air, may be derived from the production of that acid†.

Though the above experiments amply demonstrate the identity of the decompositions effected by common and voltaic electricity, the true *polar* decomposition of *water* by the former has not hitherto been so effected as to collect an appreciable portion of oxygen and hydrogen, at the positive and negative poles: Faraday's experiments, however, leave no doubt as to the reality of such decomposition. When sparks or shocks are transmitted through water by fine metallic points, streams of gas arise from them‡, but they consist of oxygen and hydrogen at each pole,

* A curious experiment, which has been called *electro-chemical*, consists in tracing lines or devices upon a thin plate of glass covered with lac varnish, with the nob of a positively charged Leyden phial; *positive* electricity is thus communicated to the side touched, and corresponding lines of *negative* electricity are produced by induction, upon the opposite side. If we now suspend the glass plate insulated in the air, and blow upon it a finely-powdered mixture of sulphur and red lead, the *latter* only will adhere to those parts of the plate which are *positively* electrified. If we now blow the same mixture upon the other side of the plate, the *sulphur* alone will adhere to the parts which are *negatively* electrified. Thus the same lines will be traced upon both sides of the glass plate, but

with different coloured powders, the *positive* lines being *red* and the *negative* *yellow*. The cause of this appears to be, that when sulphur and red lead are triturated together, the *former* *acquires positive* and the *latter negative* electricity: hence the respective powders attach themselves to those surfaces which have an electricity *opposed* to their own.

† A similar odour is observed during the decomposition of water by the voltaic current.

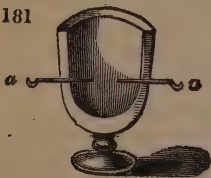
‡ This experiment was first made by the associated Dutch chemists, Van Troostwijk, and Dieman, in 1789 or earlier; it was repeated by Dr. Pearson in 1797 (*NICHOLSON'S Jour.*, 4to., i.), and afterwards by Dr. Wollaston in 1801.—(*Phil. Trans.*)

and depend upon some cause, distinct from that which regulates the transference and final place of the evolved bodies, in cases of true electrochemical decomposition.

The *physiological effects* of the common electric current may be considered the same with those of voltaic electricity, account being taken of the *intensity* of the one, and the *duration* of the other.

With regard to the *spark*, that from common electricity rivals in brilliancy the splendid light of the voltaic discharge, but it endures for the fraction of an instant only. When the voltaic and the common spark are taken between amalgamated surfaces of metal, at intervals only, and through the same distance of air, the eye can distinguish no difference between them. A curious modification of the spark of a Leyden jar or battery is obtained, by causing the electricity to pass through some distance of water or other imperfect conductor, such as a piece of wet string, so placed as to form a part of the circuit: the spark is then yellowish, flamy, of sensibly longer duration than if the water had not been interposed, and is accompanied by little or no noise; if taken between pieces of charcoal it is extremely luminous and bright upon both surfaces of the charcoal: thus, whilst losing part of its usual character, it, in some degree, approximates to the voltaic spark. The *retardation* which the current of electricity suffers in being thus made to traverse water, is well illustrated by its effect in inflaming gunpowder. In attempting to ignite gunpowder by the discharge of a Leyden jar, unless it is finely powdered and rammed into a small tube or quill, and the discharge of a large jar or battery passed through it by points of iron wire, it is generally thrown

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about but not exploded. Place the powder, for instance, in a small ivory mortar, of which fig. 181 is a section, and discharge a moderate-sized Leyden jar through it, so that the spark may pass between the interrupted wires *a a*; in this case the powder will be dispersed, and not ignited. But now repeat the experiment, placing a basin of water in the circuit, so that it may be interrupted by ten or twelve inches of that fluid, and the spark that passes under such circumstances will invariably fire the powder; or, the circuit may be interrupted

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by a few inches of pack-thread well soaked in water, and the same effect will ensue. Fig. 182 is a representation of the arrangement: *a* is a Leyden jar with a piece of chain touching its exterior coating, and immersed at the other end into the shallow dish of water *b*, from the opposite side of which another chain issues, attached to one of the conductors of the mortar *c*: a chain is also attached to the opposite con-

ductors of the mortar *c*: a chain is also attached to the opposite con-

ductor; and the discharge is effected, by bringing the ball of the discharger *d* in contact with the nob of the jar *e*. When the circuit is entirely metallic, the passage of the electricity is apparently too rapid to kindle the powder, but it does so when retarded somewhat in its progress, by being made to traverse the water.

§ 15.—ANIMAL ELECTRICITY.

THERE are some remarkable instances of the generation of electricity in living animals, to whom the power seems to be given principally as a means of defence. Of these animals, the *Torpedo* or *Electric ray*, was noticed by the ancient writers on natural history: it inhabits the Mediterranean and North Seas; its weight, when full grown, is about eighteen or twenty pounds. When touched, it communicates a benumbing sensation, and by repeated contacts, gives a series of electric shocks.

The *Gymnotus*, or *Electric eel*, was first described in 1677, by M. Richer, who was commissioned by the French Academy to make some mathematical observations in Cayenne. It is a native of the warmer regions of Africa and America, inhabiting the larger rivers, especially those of Surinam. In Africa it chiefly occurs in the branches of the Senegal. These animals have been anatomically described by Mr. Hunter in the 63rd and 65th volumes of the *Philosophical Transactions*. Their electric organs consist of membranous septa, and are most abundantly supplied by nerves; their too frequent use is succeeded by debility and death. That these organs are not otherwise essential to the animals, is shown by their thriving after they have been removed.

The *Silurus electricus* is less perfectly known: it has been described by Broussonnet under the name of *Trembleur*. (*Histoire de l'Académie Royale des Sciences*, 1782.)

Walsh, Ingenhousz, Cavendish, Sir H. Davy, and Dr. Davy, (*Phil. Trans.*, 1773, 1775, 1776, 1829, and 1832,) have each experimented on this form of electricity, and their joint results leave no doubt as to its identity with common and voltaic electricity. Mr. Faraday, availing himself of a gymnotus brought to this country by Mr. Porter, and purchased by the proprietors of the Adelaide Gallery, has instituted new inquiries respecting the electric powers of this extraordinary animal. (*Phil. Trans.*, 1838.)

Humboldt, in his *Tableau Physique des Régions Equatoriales*, &c., has given some curious details respecting the electrical eel which inhabits the rivers and lakes of the low provinces of Venezuela and the Caraccas. It is met with most frequently in the stagnant ponds dispersed at intervals over the plains which extend from the Oronoco to the Apuré. The old road near Urutica has even been abandoned, on account of the danger experienced in crossing a ford, where the mules were, from the effect of the shocks, often paralysed and drowned. Even the angler sometimes receives a stroke conveyed along his rod and line. These eels are about six feet in length, and occasion a highly painful sensation, more resembling the effect of a blow on the head than the shock of a common electric discharge; a peculiarity of effect, referable perhaps to a great

quantity of electricity of small intensity. The following particulars given also upon the authority of Humboldt (*Edin. Review*, vol. xvi. p. 250) are too curious to be here omitted.

"The Indians entertain such a dread of the *Gymnotus*, and show so much reluctance to approach it when alive and active, that Humboldt found extreme difficulty in procuring a few to serve as the subjects of experiment. For this express purpose he stopped some days on his journey across the *Llanos* to the river Apuré, at the small town of Calaboze, in the neighbourhood of which he was informed that they were very numerous. But, though his landlord took the utmost pains to gratify his wish, he was constantly unsuccessful. At last he determined to proceed himself to the spot, and was conducted to a piece of shallow water, stagnant and muddy, but of the heat of 79 degrees, surrounded by a rich vegetation of the great Indian fig-trees and odoriferous sensitive plants. Here he soon witnessed a spectacle of the most novel and extraordinary kind: about thirty horses and mules were quickly collected from the adjacent savannahs where they run half wild. These the Indians drove into the marsh. The *gymnoti*, roused from their slumbers by the noise and tumult, mount near the surface, and swimming like so many livid water-serpents, briskly pursue the intruders, and gliding under their bellies, discharge through them the most violent and repeated shocks. The horses, convulsed and terrified, their mane erect, and their eyes staring with pain and anguish, made unavailing struggles to escape. In less than five minutes two of them sunk under the water and were drowned. Victory seemed to declare for the electric eels. But their activity now began to relax. Fatigued by such expense of nervous energy, they shot their electric discharges with less frequency and effect. The surviving horses gradually recovered from the shocks, and became more composed and vigorous. In a quarter of an hour the *gymnoti* finally retired from the contest, and in such a state of languor and complete exhaustion, that they were easily dragged on shore by the help of small harpoons fastened to cords."

The *gymnotus* experimented with by Mr. Faraday gave a powerful shock when one hand was placed near each extremity of the fish. By the proper application of conductors it affected the galvanometer, and made a magnet; polar decomposition of iodide of potassium was easily effected by it, with such phenomena as indicated a current passing from the anterior to the posterior parts of the animal; and, lastly, the spark was obtained.

Those who are fond of supposing that electricity is an agent in certain processes of vitality, have referred, in favour of their hypothesis, to certain other cases of its production by arrangements of different organic substances. If the hind legs of a frog be placed upon a glass plate, and the crural nerve dissected out of one made to communicate with the other, it will be found, upon making occasional contacts with the remaining crural nerve, that the limbs of the animal will be agitated at each contact. Hence some physiologists suppose that electricity may be concerned in some of the most recondite phenomena of life, and experiments have been made tending to confer some probability on this idea.

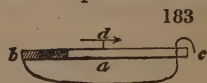
"The principle once established, that there may exist in the animal

economy a power of determining the developement of electric excitement capable of being transmitted along the nerves; and it being ascertained by numerous and decisive experiments, that the transmission of voltaic electricity along the nerves of even a dead animal is sufficient to produce the most violent muscular action, it became an easy step to refer the origin of muscular motion in the living frame to a similar cause, and to look to the brain, a wonderfully constituted organ, for which no mode of action possessing the least plausibility had ever been devised, as the source of the required electrical power."

Sir John Herschel*, from whom I have quoted the last paragraph, extends his ideas upon this subject in the following note. "If the brain be an electric pile, constantly in action, it may be conceived to discharge itself at regular intervals, when the tension of the electricity developed reaches a certain point, along the nerves which communicate with the heart, and thus to excite the pulsations of that organ. This idea is forcibly suggested by a view of that elegant apparatus, the dry pile of De Luc, in which the successive accumulations of electricity are carried off by a suspended ball, which is kept, by the discharges, in a state of regular pulsation for any length of time. We have witnessed the action of such a pile maintained in this way for whole years, in the study of the above-named eminent philosopher. The same idea of the cause of the pulsation of the heart appears to have occurred to Dr. Arnott, and is mentioned in his useful and excellent book on Physics, to which, however, we are not indebted for the suggestion, it having occurred to us, independently, many years ago."

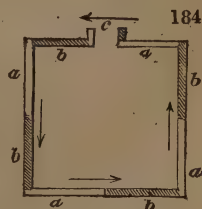
§ 16.—THERMO-ELECTRICITY.

In 1832 Professor Seebeck of Berlin discovered this form of electricity: he found that a bar of antimony, (fig. 183,) *a*, with a piece of brass wire twisted round one end of it *b*, and attached to the other in the form of a loop *c*, when heated by the flame of a spirit-lamp at the contact of the metals *b*, caused the deflection of a magnetic needle placed at *d*.



But two metals are not necessary to this effect, for if one end of the galvanometer-wire be cooled and the other heated, especially if it be of platinum, the needle will deviate when they are brought into contact. If a bar of bismuth be soldered to one end of the galvanometer-wire and a bar of antimony to the other, no effect is produced on bringing the two bars into contact when they are both of the same temperature; but if one of them be either heated or cooled, and then made to touch the other, the flowing of an electric current is immediately indicated.

This current of electricity is rendered more evident by the following modification of the arrangement; in which *a* (fig. 184) represents four bars of antimony, soldered to four bars of bismuth *b*. If the extremities at *c* be now united by perfect metallic contact, as by dipping them into



* *Preliminary Discourse on the Study of Natural Philosophy*, p. 342.

mercury, and *heat* and *cold* applied alternately to the junctions of the two metals, an electric current will be put into motion in the direction of the darts, which will deflect a magnetic needle from its meridian, placed immediately over or under any part of the circle, and which may be rendered more evident by the deflection of the galvanometer properly connected with the extremes *c.*

The term *stereo-electric* has been also applied to this current, implying its production in *solid* bodies independent of a fluid (from *στερεος*, *solid*) as opposed to the voltaic or *hydro-electric* current.

By forming circuits of the metals taken in pairs, they may be arranged in a series descending from the extreme negative, which is bismuth, to the extreme positive, antimony. Their thermo-electric properties have no correspondence either with their voltaic relations, or powers of conducting heat, or electricity; neither do they accord with specific gravity, nor atomic weights. These relations are shown in the following table from Professor CUMMING'S *Manual of Electro-dynamics*, every substance in the thermo-electric series being considered as negative to all below, and positive to all above: hence, any metal in the upper part will form a circuit with all below it, similar to, though less powerful than, that of bismuth and antimony. Dr. Roget, in his treatise on *electro-magnetism* (in the *Library of Useful Knowledge*, p. 94) inverts these terms, and says, that in the following thermo-electric series, every metal is positive to those below it, and negative to those above: in the deflection of the needle, bismuth and antimony bear the same relation to each other as silver and zinc in the single voltaic circuit, hence it flows from the antimony to the bismuth; the latter, therefore, corresponds to the positive, and the former to the negative element: in this acceptation, therefore, Dr. Roget is correct: in the compound voltaic series, when the zinc end is called the *positive*, and the copper the *negative* pole, the terms are of course reversed.

THERMO-ELECTRIC VOLTAIC SERIES

SERIES.	by acids.
Galena	Potassium
Bismuth	Barium
Mercury	Zinc
Nickel	Cadmium
Platinum	Tin
Palladium	Iron
Cobalt	Bismuth
Manganese	Antimony
Tin	Lead
Lead	Copper
Brass	Silver
Rhodium	Palladium
Gold	Tellurium
Copper	Gold
Silver	Charcoal
Zinc	Platinum
Cadmium	Iridium
Charcoal	Rhodium
Plumbago	
Iron	
Arsenic	
Antimony	

SERIES OF CONDUCTORS,

of Electricity.	of Heat.
Silver	Silver
Copper	Gold
Lead	Tin
Gold	Copper
Brass	Platinum
Zinc	Iron
Tin	Lead
Platinum	
Palladium	
Iron	

According to the experiments of Nobili, thermo-electric circuits may be formed with substances of lower conducting powers than the metals. He made small cylinders of porcelain clay, and wrapped round the end of each some cotton steeped in a conducting liquid, which served to place them in direct communication with a galvanometer: one of the ends was reduced to a point, and after heating it to redness by a spirit-lamp, was pressed on the cold extremity of the other cylinder, when a current was established from the hot to the cold part of the arrangement.

All the phenomena of the thermo-electric current show it to depend upon considerable *quantity* opposed to very feeble *intensity*; it is indeed apparently sluggish even in its passage through metals; in that respect therefore directly opposed to common electricity. It is not easily cognizable by any means except the deflection of the magnetic needle, and has not hitherto been made to produce heat, or light, or chemical effects, though it is said to have convulsed the limb of a frog (NOBILI, *Bib. Univ.*, xxxvii., 15). A beautiful application of a thermo-electrical apparatus has been made by Nobili and Melloni (*Bull. des Sciences*, 1831), and employed by the latter in his experiments on radiant heat: they constructed a *thermo-electric pile* of thirty-six pairs of small plates of bismuth and antimony, and attached it to a delicate galvanometer: it was so susceptible of changes of temperature, and, therefore, so delicate a *thermoscope*, as to be affected by the warmth of the hand held at a considerable distance from it: in experiments on radiant heat it is rendered additionally sensible by covering one of its faces with a thin coating of lamp-black.

Some theorists have adduced the phenomena of thermo-electricity in support of the contact-theory of the pile, but Faraday's arguments and experiments prove that the two series of phenomena are perfectly distinct; a conclusion also sanctioned by the researches of Becquerel. (*Phil. Trans.* 1840, p. 122, *Ann. Ch. et Ph.*, xli. 355, xlv. 275*.)

* Some extraordinary phenomena, in some respects the converse of those which we have called thermo-electric, have been observed by Peltier. When a weak electric current from a single circuit is transmitted through a bar of equal lengths of bismuth and antimony soldered together, from the antimony to the bismuth, heat is evolved at the point of junction, but if in the contrary direction, cold. The effects are appreciable by placing the bulb of a delicate thermometer in a hole at the point of junction; it rises 80° in the first case, and sinks to 6° in the second. If the bar be placed on thawing ice, a little water may thus be frozen in the cavity made for the thermometer.

"This production of cold by the voltaic current may be demonstrated also in a striking way by the secondary thermo-electric current which it tends to generate. Let a bar of bismuth 4·5 inches long, 0·4 inch square, and a similar bar of antimony be placed across each other at

right angles, and mortice half their thicknesses into each other at the place where they cross, and solder them together with tin. On connecting two of their ends with a galvanometer, and sending a current through the others, a deflection of the needle will take place on one side from the current generated by the change of temperature; when the direction of the current is reversed, the needle will be deflected in the contrary direction, proving that an opposite change of temperature has taken place from the reversal of the current. That this secondary current is not due to any diversion of the primary current, may be proved by connecting the two ends of the same bar with the galvanometer, and sending the current through the other bar, when no effect will be produced.

"These effects of what may, perhaps, be designated as *electro-thermancy*, which we owe to M. Peltier, are the converse of those of thermo-electricity." DANIELL'S *Introduction*, § 800.

§ 17.—MAGNETISM.

THERE are certain native oxides of iron which are termed *magnetic iron ores*, and which have the remarkable property of attracting iron filings: when, or by whom this property was originally discovered, is not known; but the Greeks called the iron ore *μαγνητος*, from the name, as it is said, of a shepherd, who first observed it. Pliny describes it under the name of *magnes*, a term said to be derived from Magnesia, a province of Lydia, where this ore abounded.

If a bar of *tempered steel* be rubbed in a certain direction with this native magnet, or *loadstone*, it is itself rendered *permanently magnetic*, and acquires properties similar to those of its source.

There are other means by which magnetism may be temporarily or permanently conferred on iron, and even on other metals; but steel is the only substance (with the exception of nickel) which receives and retains it*: of these sources of magnetism, *electricity* is among the most remarkable, and a new branch of science has arisen out of the phenomena thus presented, called *electro-magnetism*; it is to render the details upon this subject intelligible, that I shall here briefly describe the leading properties of the common magnet, without, however, entering into the extended and interesting theoretical reasonings which have been founded upon them, and which refer to the ultimate *cause* of this important and recondite property†.

The most obvious properties of the magnet are—1, polarity; 2, attraction of iron; 3, attraction and repulsion of another magnet; and, 4, the production of magnetism in iron by induction.

1. POLARITY.—If a slender bar, or needle, of steel rendered magnetic, be poised on a central point, or suspended by a thread so as to have perfectly free motion in a horizontal plane, and to be uninfluenced by neighbouring ferruginous bodies, it will for a time oscillate to and fro, and ultimately settle in a position nearly *north and south*; and if again disturbed, it will vibrate, and again assume the same direction, which, therefore, is called the *magnetic meridian*; this constitutes *magnetic polarity*, and the ends of the needle pointing north and south are usually called its *north and south poles*.

2. ATTRACTION OF IRON.—On bringing either pole of a magnet near a small piece of iron, it will be attracted; and if iron-filings are used, they will cluster about the poles. From the way in which the filings

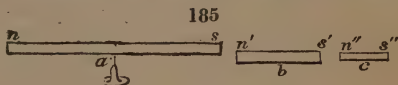
* In making a magnet, a bar of steel is rubbed in *one direction* by a magnet: great care is necessary in observing the direction, and not reversing it, for a powerful magnet may be presently unmade, or rendered unmagnetic, by passing a magnet over it in an opposite direction to that in which its magnetism had originally been conferred. A good abstract of the methods of making artificial magnets, will be found in the *Library of Useful Knowledge*, (Magnetism, p. 41.)

† The compendium of magnetism and electro-magnetism by Dr. Roget, in the *Library of Useful Knowledge*, Professor Cumming's *Manual of Electrodynamics*, the articles on "Magnetism" in the *Encyclopædia Metropolitana*, and the papers of Professor Faraday in the *Phil. Trans.*, are the authorities to which I refer those who wish for information upon the above subjects, and for particulars incompatible with the object of this *Manual*.

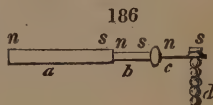
adhere, it appears that in the common magnetic needle, the great attractive force is near its extreme ends, or at its *poles*, and that it diminishes towards the centre, at or near which no attraction exists. These attractions are *mutual*, that is, the iron attracts the magnet, and *vice versâ*.

3. ATTRACTION AND REPULSION OF ANOTHER MAGNET.—If we bring the pole of another magnet near that which is poised, we shall find that if the two *similar* poles be presented to each other, they exhibit a mutual *repulsion*; but that the *dissimilar* poles, mutually attract each other; here, therefore, we observe an analogy between magnetism and electricity, for *between similar powers there is repulsion, and between dissimilar powers, attraction*.

4. MAGNETIC INDUCTION.—If a bar of iron be brought near a magnet, the iron acquires temporary, or *induced magnetism*; and here again an analogy to electric induction will be observed. Let *a*, fig. 185, represent a bar magnet, and *b* a bar of unmagnetic and *soft iron*, brought to within a short distance of *s*, the south pole of *a*: it will then be found, that whilst in this situation *b* is a magnet, the poles of which, *n' s'*, are opposed to those of *a*, and consequently attraction subsists between *s* and *n'*; and if a second piece of soft iron, *c*, be placed near *b*, it will also become polar, *n''* being its north, and *s''* its south pole, consequently *s'* and *n''* will attract each other; on withdrawing *a* all magnetic properties in *b* and *c* immediately vanish.



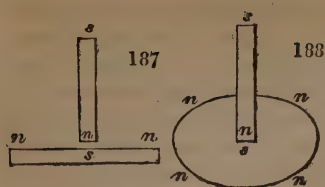
The experiment may be modified, as shown in fig. 186, where *a* is the magnet, *b* a short bar of iron, *c* an iron key, and *d* several iron bullets; the magnetism in *b*, *c*, and *d* is here *induced* by *a*; the respective north and south poles are produced and attracted as before, and each bullet acquires a similar polarity by which they are mutually held together; if *a* be now carefully withdrawn to within a very short distance of *b*, *b c* and *d* will still retain their induced magnetism; but, on removing *a* to a greater distance, *b c* and *d* will drop asunder, and all magnetism disappear. When, therefore, a cluster of iron-filings is held by the pole of a magnet, each particle of iron is polar, and the whole is an analogous result of induction.



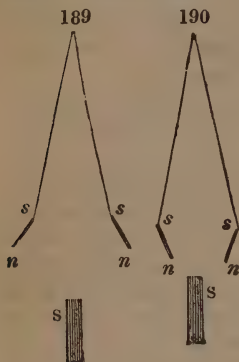
It has been observed that when a magnet is acting upon a piece of soft iron by induction, as in the case of *a* and *b*, fig. 185, the power or intensity of the magnetism in *a* suffers an increase, and its poles, whilst under induction, have a greater attractive power, and will sustain a greater weight than when that influence is removed.

According to Mr. Harris, the intensity of magnetic power developed by induction in an iron bar, is inversely as the distance of the inducing pole from the adjacent end of the bar on which it acts; and the intensity of magnetism induced on the remote end of the bar is, with the same inductive power acting on the nearer end, inversely as the length of the bar. (*Trans. R. S. Edin.*, 1829.)

When a magnet, instead of being applied as in fig. 185 to the *end* of an iron bar, is applied to its *centre* (fig. 187), both the extremities assume



and every part of the *circumference* will acquire the properties of a weak *north pole*, as in fig. 188. The following simple experiment furnishes a useful illustration of the phenomena of induction and of magnetic



attraction and repulsion. Attach two short pieces of iron-wire to a thread, and suspend them opposite to each other as in fig. 189. Then bring the pole of the magnet, *s*, slowly towards them; the wires will gradually *diverge* because they become magnetic by induction, and their north poles *nn*, and south poles *ss*, are thus rendered similarly magnetic; but, on advancing the pole of the magnet nearer to the wires, as in fig. 190, its attractive power overcomes the repulsion that exists between the ends *nn*, and they are consequently *drawn towards s*, while the repulsion between *ss* is increased. It is upon this principle that the

filaments of polar iron-filings adhering to the pole of a strong magnet, diverge, or are repelled by each other.

All the magnetic properties induced in soft iron cease when it is heated to bright redness; so that if we heat the whole of a small iron bar up to that point, and then bring it near a magnetic needle, it will not affect it; as soon as it is cooled down to a common red heat the magnetism returns, and is stronger than in the cold iron: but there is one particular period during cooling, between the white and red heat, at which the induced polarity is inverted; or in which the iron attracts the needle the contrary way to what it does when it is cold. (BARLOW, *Phil. Trans.* 1822, p. 118.) We also find that the permanent magnetism of a steel needle is diminished by a moderate heat, and that a red heat totally destroys it. Mr. Faraday found the induced magnetism of nickel to be destroyed by a heat below redness, and conceives it probable that the unmagnetic metals are, at *common temperatures*, in the same relation to magnetism as iron at a *bright red heat*, and that at some very low temperature they would exhibit a similar relation to magnetism with that belonging to iron at common temperatures*.

It is obvious, from the position assumed by the magnetic needle when freely moving in an horizontal plane, that there is some attractive force in the earth, which causes it to assume a constant direction, and that what we have termed the north pole of the magnet, is attracted towards the north pole of the earth, and its south pole by the south pole

* In reference to the influence of *temperature* upon magnetism, see a paper by Mr. Christie. (*Phil. Trans.*, 1825.)

of the earth; and hence it is inferred, according to the above stated law of magnetic attraction, that the poles of the earth are in an opposite magnetic state to those of the needle.

We find that the earth has a further influence upon an artificial magnet, which is only rendered evident when it is so suspended as to move freely in every direction. Under these circumstances, and in our latitudes, the *north pole* of the needle is attracted *downwards*, as well as to the north, and assumes a position almost vertical, that is, making an angle with the plumb line of about 20° : this inclination to the horizontal plane is called the *dip of the magnetic needle*.

These, and other phenomena, have been ascribed to the influence of a magnetic power in the earth: Dr. Halley regarded the globe as constituting a great magnet having four poles, two to the north and two to the south, at considerable and unequal distances from the poles of the earth. (*Miscellanea Curiosa*: as quoted by Dr. THOMSON on *Heat and Electricity*, p. 546.) Two of these poles, one to the north and one to the south, are supposed to be *fixed*, the other two *moveable*. M. Hansteen has adopted a similar hypothesis, and the changes in the direction and dip of the needle, or the *variation of the compass*, have been referred to such causes*: these, however, are subjects which it is unnecessary to pursue here, and I have only thus far adverted to them, to remind the student of the necessity of taking the influence of the earth's magnetism into the account, in all cases where we speak of this power, and to explain another cause of the temporary and permanent production of magnetism in iron and steel, resulting exclusively from the earth's influence.

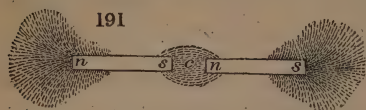
When a bar of soft iron is held nearly *vertical*, or in the *direction of the dipping needle*, its ends are no longer *indifferently* attractive of a poised magnet; but (so long only as it continues in or near that position) it is *polar*, the *lower end* of the bar being a *north pole*, and the *upper end* a *south pole*, and it affects the magnetic needle accordingly. We now need only place the bar in a *horizontal* position, and both ends then *indifferently* attract the poles of the needle; or in other words, the induction of the earth is *neutralized* and vanishes. It is not uncommon to find bars of steel, which have long remained in a nearly vertical position, permanently magnetic; that is, *polar*; this is often the case with the poker and tongs: and there is a very curious mode of making a magnet, dependent upon the same cause, which consists in holding a bar of steel in the direction of the magnetic dip, and striking it whilst in that position, a few smart blows with a hammer: the upper and lower ends then become south and north poles. If a bar of steel already magnetized, and not in this position, be similarly treated, it loses its magnetism: and hence the necessity of caution in using good magnets, to

* In the year 1660, the magnetic needle in London pointed exactly north and south, London being at that time in the *line of no variation*. Before that period, the variation was to the east, but after the year 1660, the variation became westerly, the line of no variation therefore has been progressively but slowly moving in a westerly direction, and has

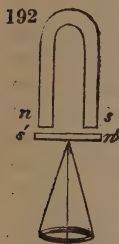
now passed to North America. At London, the westerly variation continued to increase till 1818, when it amounted to $24^{\circ} 30'$; this appears to have been its maximum, and since that time it has somewhat diminished. The *dip* has undergone corresponding changes: in 1773 the dip was $72^{\circ} 19'$; in 1830, $69^{\circ} 38'$.

avoid striking them or letting them fall, by which their magnetism is more or less weakened.

The manner in which the magnetic force emanates from the poles of a magnet is well illustrated, by placing two magnetized bars with their opposite poles about an inch asunder, under a sheet of writing-paper, and then sifting iron filings upon the paper; they will assume a peculiar and beautiful arrangement, showing the direction of the *magnetic curves*, (some-



what as in the annexed figure 191,) which is perfected by gently shaking or tapping the paper to assist their polar adhesions. If we place a piece of soft iron between the poles, and within the curves at *c*, it becomes, as already explained, magnetic, by induction. These curves or currents are well shown between the poles of what is commonly called a *horse-shoe magnet*, in which the magnetized bar is bent into that form (fig. 192). *ns* are its north and south poles; *s'n'* are the *induced* north and south poles of a bar of soft iron, commonly called the *holder*, and which, when applied to the magnet, is powerfully attracted. A scale may be conveniently attached to the holder for determining the power of the magnet by the weight which it will sustain.



As iron and steel, when free from magnetism, are attracted only in consequence of induction, it follows that the degree of susceptibility to induction may be measured by the attraction which results from this property. With this view, Mr. Barlow (*Phil Trans.*, 1822, p. 117) made a series of experiments to ascertain the relative attraction which different species of iron and steel had for the magnet, and obtained the following results, the relative magnetic power of each substance being expressed by numbers.

Malleable-iron	100	Hard blistered-steel	53
Soft cast-steel	74	Hard shear-steel	53
Soft blistered-steel	67	Hard cast-steel	49
Soft shear-steel	66	Cast-iron	48

Mr. Hatchett found that the *protosulphuret* and *phosphuret* of iron, were susceptible of receiving and retaining magnetism; in this respect, therefore, they resemble the *protoxides* of that metal, and the *protocarburet*, or steel: the peroxides, the persulphurets, and plumbago, natural and artificial, are not magnetic: his suggestions, in reference to the magnetic properties of the above compounds, and of the circumstances which interfere with those of the varieties of cast-iron, deserve further consideration.—(*Phil. Trans.*, 1804.)

§ 18.—ELECTRO-MAGNETISM*.

HAVING, in the preceding section, defined the meaning of the term *magnetism*, we now proceed to examine the *evolution of magnetism* by

* The reader who may be desirous of historical details and references to authors, upon this subject, may advantageously consult Mr. Faraday's "Historical Sketch of Electro-magnetism," in the *Annals of Philosophy*.—(New Series. ii.)

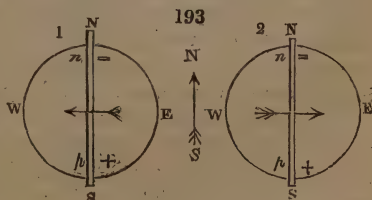
electricity; this important discovery was made in 1819, by Professor Ørsted of Copenhagen.

All the effects we are about to describe depend entirely upon *electricity in motion*, or upon *electric currents*, and are directly proportionate to the *quantity* of electricity: nothing of the kind is produced by electricity of *tension*, nor are they apparently increased by increasing the *intensity* of the current. Hence, for their developement, voltaic electricity is infinitely more effective than common electricity; and in the voltaic arrangements employed, all depends upon the *surface of the plates*, and nothing upon the number of their alternations: hence also *perfect metallic contact* of the conductors employed must be observed.

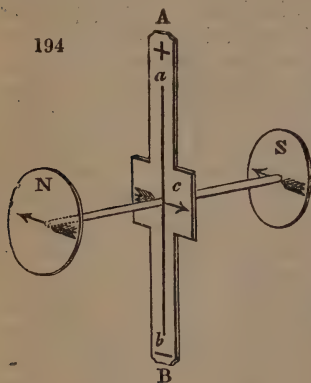
When a wire transmitting the volta-electric current (and which may be called the *connecting wire*) is brought near a common magnetic needle, it has the power of attracting and repelling it, in obedience to very peculiar laws. If a magnetic needle be left to take its natural direction, and then a straight portion of the connecting wire be brought *above and parallel to it*, the end of the needle which is next the negative pole of the battery moves towards the *west*, and that, whether the wire be on the one or other side of the needle, so that it be above and parallel to it. If the connecting wire be sunk on either side of the needle, so as to come into the *horizontal plane* in which the needle is allowed to move, there is no motion of the needle in that plane, but the pole of the needle attempts to move in a *vertical circle*, and but for the imperfect suspension, and the earth's magnetism, would do so. When this wire is on the *east* of the needle, the pole next the negative end of the battery is *elevated*, and when on the *west* of the needle it is *depressed*. If the connecting wire be now sunk *below the level of the needle*, similar attractions and repulsions take place, but in opposite directions to those followed when it is above. The pole of the needle opposite the negative end of the battery now moves *eastwards*, whatever the position of the wire, so that it be restricted as above.

In discussing the relations of the electric and magnetic currents indicated by this experiment, it may be useful, instead of indiscriminately using the terms north and south, east and west, and negative and positive, to employ them in reference to the following position. If we stand with the face towards the north, and the current of electricity pass in the same direction, that is from the south to the north (parallel with the magnetic meridian) then the magnetic needle, when *above* the electric current, will turn to the *left*, or to the *west*; and *below* the current, to the *right* or to the *east*: its north pole will be *elevated* when on the *east* side of the current, and *depressed* when upon the *west*, and will have a tendency, therefore, to *revolve* round the electric current in a direction from *east to west*, or from *right to left*.

In the diagram (fig. 193) the electric current is supposed passing through the conducting-wire *p n* (1), in the direction *s N*, in which case the magnetic needle, placed *above* it, has its marked or north pole deflected towards the *west*, and (as in 2), placed *below* it, towards the *east*.



The following contrivance of Dr. Roget is useful in assisting the memory respecting the details of these affections. A B (fig. 194) is a slip of card, on each side of which a line $a b$ is drawn along the middle of its length, the end a being marked +, the end b —, and the centre c , being crossed by an arrow at right angles to it, directed as in the figure. Through the centre and at right angles to the plane of the slip of card, there is made to pass a slender stem of wood, at the two ends of which are fixed in planes parallel to the slip of card A B, the circular discs of card, marked respectively with the letters N and S, and with arrows parallel to, but pointing in a contrary direction to the one at c . The same marks must be put on the reverse of each of the three pieces of card, so that when held in different situations they may be seen without turning the instrument.



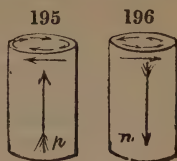
If the line $a b$ be supposed to represent the galvanic wire (the direction of the current of electricity being denoted by the signs + and —, at the ends of the line), the arrow at the centre will point out the direction in which it tends to move, when under the influence of the north pole of a magnet, situated at N; or of a south pole situated on the other side at S: and *vice versâ*, the arrows at N and S will indicate the directions in which the north and south pole, respectively, tends to revolve round the galvanized wire in its vicinity, with relation to the direction of the current of electricity that is passing through it.

It must be observed that the poles N and S are here not considered as in connexion with each other, or as forming parts of one magnet: their operations are exhibited singly, and quite independently of each other. The advantage of this little instrument consists in its being capable of being held in any situation, and thus easily adapted to the circumstances of any fact or experiment of which we may wish to examine the theory.

All substances, which admit of the transfer of the electric current, exhibit similar phenomena; but the best conductors, or those which appear to afford the least resistance to the current, are those which become most powerfully magnetic: the metals, therefore, stand in the order of their electro-conductive powers; and when liquids are used, the best conductors among them are those by which the magnetic needle is most powerfully affected. The electric current itself, when passing through rare air, exhibits the same phenomena. Every part of the conductor, of course, exhibits similar phenomena, and everything through which the current is passing; the connecting-wire, therefore, so long as the current is passing through it, is everywhere attractive of iron-filings, and the voltaic pile itself acts upon the needle, precisely as the connecting-wire.

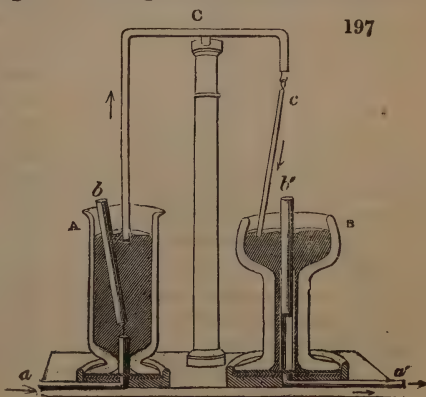
From the manner in which the needle is affected when placed parallel to either side of the electric current, it was inferred that a current of magnetism (as it may be termed) is put into motion by the electric current, so as to circulate, as it were, at right angles to the latter: hence

Dr. Wollaston termed it *vertiginous magnetism*; or, as Mr. Barlow expressed it, the magnetic force exerts a *tangential* action. Let us, therefore, suppose fig. 195 to represent the conductor through which the electric current is passing from end to end in the direction of the dart *p*, then the small arrows will represent the direction of the circulating current of magnetism. In fig. 196 both currents are moving in the opposite direction. Supposing the wires or conductors above represented placed side by side and parallel to each other, they will obviously be *magnetically repulsive*, because similar magnetic polarities (as shown by the horizontal darts) are opposed to each other; but if we invert either conductor, or, what amounts to the same thing, change the direction of the electric current in it, they will then become *magnetically attractive*, because the dissimilar magnetic polarities are then opposed to each other. So that two wires in which the electric current is passing in the same direction are magnetically attractive; and two wires, in which the electric current is passing in opposite directions, are magnetically repulsive.



Impressed with this view of the relative motions of the electric and magnetic currents, Mr. Faraday conceived that the pole of the magnet ought to revolve about the electric conductor, and the electric conductor about the pole of the magnet, and by the following very ingenious apparatus he succeeded in the experimental verification of the theory*.

Fig. 197 represents two glass vessels, A and B, placed side by side, with their appendages. In A the motion of a magnetic pole round the connecting-wire (or electric current) is produced, and in B the connecting-wire moves round the pole of the magnet. That a current of electricity may be established through the cup A, a hole is drilled at the bottom, and into this a copper pin is ground tight, which projects into the cup, and is rivetted below to a small round plate of copper, which forms part of the foot of the vessel, and communicates with the connecting-wire *a*. A small cylindrical and powerful magnet *b* has a piece of thread fastened to one of its poles, by which it is attached to the copper pin at the bottom of the cup, and so adjusted, that when the cup is full of clean mercury, the free pole *b* floats almost upright at the surface. The stem of the vessel B is tubular, and a copper socket is attached to its copper foot, in connexion with the conductor *a'*, which holds the magnet, *b'*, projecting above the centre of the mercury. In these cups of mercury, therefore, the two magnets are similarly arranged,

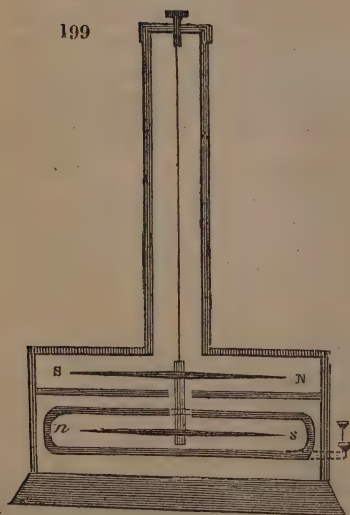
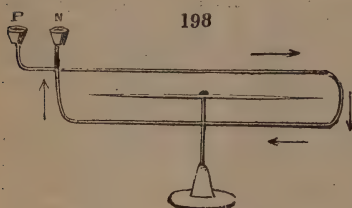


* Mr. Faraday's original papers on this subject will be found in the *Quarterly Journal of Science and the Arts*, vol. xii.,

pp. 75, 186, 283, and 416. The date of the first is September 11, 1821.

except that in A the pole is moveable, and in B, fixed. *c* is a brass stem and cross-wire prolonged by a smaller wire into the cup of mercury A, on one side, and on the other into B, but on this side the conducting-wire *c* is suspended by a loop, so as freely to move round the end of the magnet *b'*. If *a* be now connected with the positive, and *a'* with the negative, voltaic wire, so that the electric current may traverse the apparatus in the direction of the darts, the moveable magnetic pole *b* will revolve about the fixed conductor; and the moveable conductor *c* will revolve about the fixed magnetic pole *b'*. On changing the direction of the electric current, that of the respective rotatory motions will also be changed.

Since this discovery, a great variety of rotatory electro-magnetic apparatus has been suggested and contrived, in which the electric and magnetic currents are mutually made to produce the revolutions of conductors about each other, and about their own axes, in most of which volta-electricity, and in some, thermo-electricity is used: of these, a good account will be found in the *Library of Useful Knowledge* already quoted, and in Mr. F. Watkins' popular sketch of electro-magnetism and electro-dynamics.

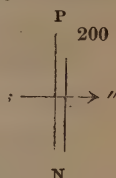


Referring to the statement just given of the manner in which the magnetic needle is affected by the electric current, the construction and use of that valuable instrument the *galvanometer*, which has been so often referred to, and which was originally suggested by Schweigger, will easily be understood. In its simplest form it consists of a magnetic needle, so poised as to be affected by an electric current passing above and below it, as in fig. 198, where *P* and *N* are two small copper cups, each containing a little mercury, for the purpose of connexion with the voltaic or other source of the electric current, which moving in opposite directions in the upper and lower portions of the wire, as shown by the darts, will conspire in both cases, to deflect the needle from its natural position, in the same direction, and to bring it into a position nearer to a right angle to the plane of the wires. To multiply this effect, and to render the instrument a more susceptible indicator of feeble electric currents, the convolutions of the wire are multiplied, and the

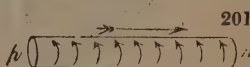
lateral transfer of electricity prevented, by coating it with silk, or sealing-wax; and instead of supporting the needle upon a pivot, it is suspended by a fine thread of silk, or, as suggested by Professor Ritchie, (*Phil.*

Trans., 1830, p. 218,) by a filament of spun-glass; the sensibility of the instrument is further increased by employing two needles, one above and the other within the coil, and placed parallel, but with their poles opposed, so as to neutralize the magnetic influence of the earth: to this instrument a divided circle is so attached as to enable the observer readily to read off the deviation. This form of galvanometer, or *electro-magnetic multiplier*, is shown in fig. 199 (in section), *ns* is the lower needle, surrounded by the coil of wire, and connected with the upper needle, *s n*, by an intermediate piece of straw, which passes through the upper part of the horizontal coil, and through the circular card above it, on which the graduated circle is drawn, and is attached to the torsion filament suspended from a screw, supported by the frame of the instrument*.

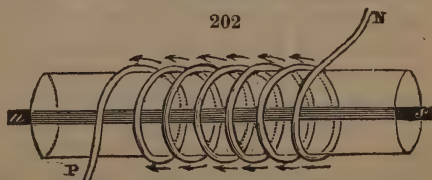
From the direction of the *magnetic* as opposed to the *electric* current, it is obvious that an iron or steel needle placed *transversely* to the connecting-wire, as in fig. 200, will acquire magnetic *polarity*, and that if *p n* represent the conducting-wire, and *s n* the needle, the nature of its polarity will depend upon its being *above* or *below* the electric current. But in thus making a magnet, either temporarily of iron, or permanently of steel, a great increase of power is obtained by winding the connecting-wire (which in this case must be covered with silk to prevent contact of the metallic surfaces) round the iron bar, in the form of a close spiral, the effect of which will be, in the first place, a close assimilation in the coil itself to a magnetic needle, and in the next a great increase in the general magnetic effect, as will be apparent from the following considerations. Let *p n*, fig. 201,



represent a straight conducting-wire, in which an electric current is passing in the direction of the large dart; the small darts, will then show the direction of the magnetic influence or vortex: if we now coil this wire into a spiral, the magnetism will tend the same way in each convolution, as in fig. 202, where the connecting-wire, (in which the direction of the *magnetic* current is indicated by the darts,) is supposed to be wound spirally round a glass tube, and where *ns* represents a

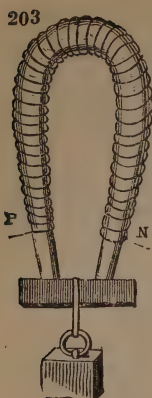


steel bar in the axis of the tube and spiral, in which case it becomes a powerful magnet. If a glass tube thus surrounded by a coil of wire traversed by the electric current be held *vertically*, it will actually draw up an iron needle and retain it in its axis, against the force of gravity.



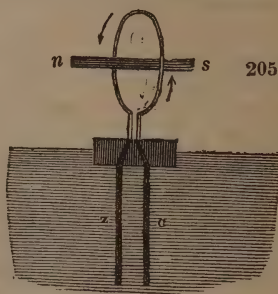
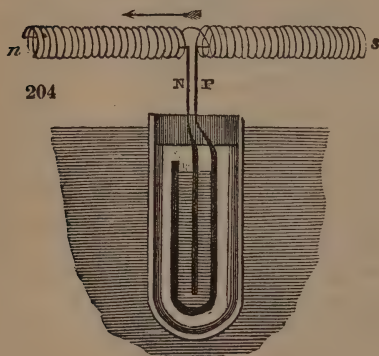
If such a wire be wound round a bar of soft iron, it is rendered a very powerful magnet during the passage of the electric current; and by employing a bent bar of iron, (fig. 203,) and connecting the extremes of the wire *p* and *n* with the positive and negative mercurial cups of the

* The various forms of the galvanometer have been improved in their mechanical arrangement by Mr. Watkins, of Charing-cross.



single voltaic plates shown in fig. 149, a most powerful form of the horseshoe magnet is obtained.

From the description of the heliacal or spiral arrangement just given, we can understand how a voltaic magnet may exactly resemble a common magnet, in its obedience to other magnets and to the earth's polarity. This is well shown in De la Rive's *floating electro-magnet* (fig. 204), in which the copper cup and zinc plate forming the simple voltaic circle, is inserted into a glass cylinder adapted for floating in water: the ends of the spiral being soldered to the wires *N P*. Here the spiral represents the magnetic needle, placing itself in the magnetic meridian, and being obedient to another magnet brought to either of its poles.

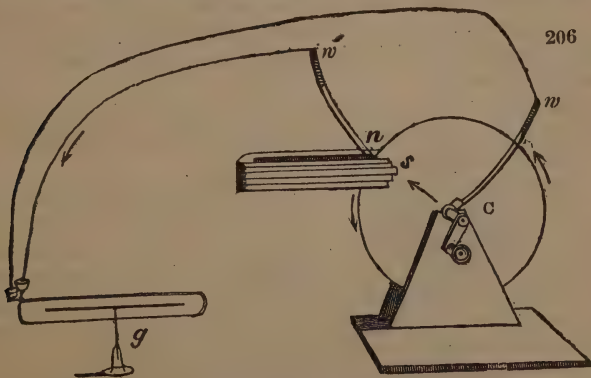


We have an interesting modification of this apparatus in De la Rive's single or circular magnetic coil, which may be constructed as follows. *z c* (fig. 205) are a zinc and copper plate attached to a piece of cork sufficient to float the whole apparatus, with the plates immersed in a basin of dilute sulphuric acid. A copper wire is soldered to the copper plate, and being covered with silk thread is formed into six or eight circular convolutions, its other end being soldered to the zinc plate. When this arrangement is floating in dilute acid, a current of electricity traverses the circles of wire in the direction of the darts, and a magnet *n s* presented horizontally to its axis causes the ring to move towards it, till it reaches its centre, where it pauses in a state of equilibrium. If we now withdraw the magnet, and reversing its poles, (whilst the ring is held in its first position,) pass it half way through the ring, it may possibly again remain in equilibrium, but the slightest change of position causes it to move with an accelerated velocity towards the pole nearest to it, and getting clear of the magnet is first repelled, then turning round so as to present its opposite face to the magnet, it is attracted, and passing again over the pole of the magnet, rests in equilibrium at its centre, or at what may be called the magnetic equator. In the first position it was equally attracted by the two poles, and in the second equally repelled.

§ 19.—MAGNETO-ELECTRICITY*.

UNDER this term, I shall describe another branch of electrical science, vying in interest and importance with the discovery of Ørsted detailed in the last section, and being in fact the converse of it, namely *the production of electricity by magnetism*, for which we are exclusively indebted to Mr. Faraday. (*Phil. Trans.*, 1831.)

From the statements in the last section, it is evident that magnetism is in some way produced by electricity in motion; now it occurred to Mr. Faraday, in consequence of certain phenomena which he observed, and which he has described under the terms *volta-electric*, and *magneto-electric induction*, that magnetism in motion ought to produce an electric current, and he succeeded in verifying this important conclusion as follows: a long spiral coil of copper-wire, covered as in the former experiments with silk, was connected by its extremities with the galvanometer, the deflection of which would of course announce a current of electricity in the spiral and wires connected with it: he now found, that in the act of introducing the pole of a powerful bar-magnet within the coils of the spiral, a deflection of the galvanometer took place in one direction, and in the act of withdrawing it took place in the opposite direction; so that each time the conducting-wire cut the magnetic curves, a current of electricity was, for the moment, produced in it. He afterwards devised the following curious modification of this experiment: c (fig. 206) is a copper plate so mounted as to admit of revolving upon



its axis; *n s* are the poles of a powerful horse-shoe magnet, so placed as to admit of the revolution of the circumference of the plate between them; *w w'* are conducting wires, one of which is retained in perfect metallic contact with the axis, and the other with the circumference of the plate at the point between the poles *n s*. These wires terminate in the galva-

* Any extended details upon this extremely curious subject would be misplaced in a *Manual of Chemistry*: I must, therefore, refer for them to Mr. Faraday's first series of experimental researches in electricity, read before the Royal Society, on the 24th of November, 1831, and published in the *Phil. Trans.* for 1832, p. 125.

nometer g. When the copper plate is made to revolve from right to left, a current of electricity is produced, in the direction of the arrows, and deflects the galvanometer accordingly. If the revolutions of the plate, or the poles of the magnet be reversed, the electric current moves in the opposite direction*.

Mr. Faraday not only succeeded in obtaining galvanometrical indications of an electric current, but, by another modification of the arrangement in which the electric current was induced by an electro-magnet, he actually succeeded in obtaining the electric spark. (*Phil. Trans.*, 1832, p. 132.) The electric spark was afterwards obtained from a common magnet, by Nobili and Antinori, and in this country by Professor Forbes. (*Phil. Trans. Edinb.*, 1832.) For this purpose, a helix of copper wire was formed round the middle of the soft iron holder of a powerful horse-shoe magnet; on making and breaking the contact between the holder and the magnet, magnetism was alternately created and destroyed within it; at these periods of transition, electric currents were induced in the helix, and on so arranging the conducting-wires as at these moments to make and break contact with mercury, a brilliant spark was observed at each motion of the holder. By making the poles of a powerful horse-shoe magnet revolve rapidly before a soft iron armature supplied as in the former case with a helix, or what is still better, causing the armature and helix to revolve before the poles, an electric current is obtained, which not only gives continuous sparks, but ignites wire, decomposes water, and produces powerful shocks. These *magneto-electric machines* whilst they furnish a beautiful illustration of the production of electricity by moving magnetism, seem also to promise some advantage in the medical applications of electricity, and have been elegantly applied to the purpose of obtaining instantaneous light, by causing the spark to inflame the wick of a small spirit-lamp.

The best form of the magneto-electric machine is that contrived by Mr. Saxton, which has been figured and described by Mr. Daniell, (*Introduction*, § 834,) as follows:—

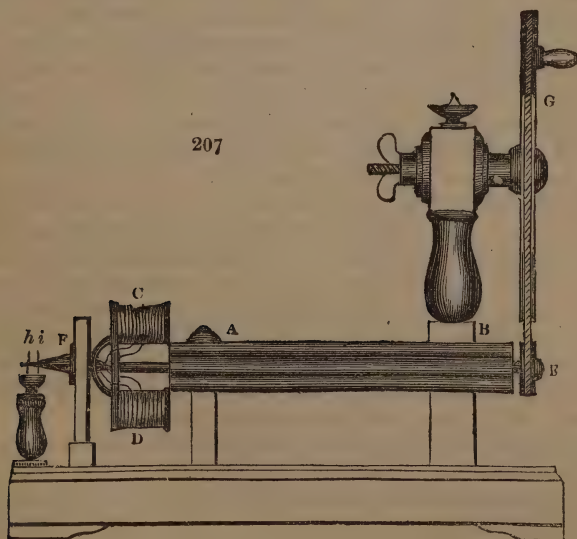
“A very powerful horse-shoe magnet, formed of numerous steel plates closely applied together, or an electro-magnet of soft iron of the same form, is placed in a horizontal position. An armature or bar of the purest soft iron has each of its ends bent at a right angle, and is mounted in such a way that the surfaces of those ends are directly opposed, and close to the poles of the magnet; in this position it may be made to rotate rapidly in a vertical direction, by means of multiplying wheels and an endless band. Two series of copper-wires, covered with silk, are wound round either end of this bar, as compound helices. The extremities of these wires having the same direction, are connected together, and with a small circular disc

* In the year 1824, M. Arago discovered that a magnet suspended over, and parallel to the surfaces of a horizontal rotating copper plate, acquired a tendency to revolve in the same direction with the plate; and also that a rotatory magnet tended to give a similar rotatory motion to a contiguous disc of copper.

—(*Phil. Trans.*, 1825, p. 467.) These phenomena are explained by the electric currents induced in the copper plate by its rotation within the magnetic curves, which currents flow at right angles to the direction of the motion. (FARADAY, *Phil. Trans.*, 1832, p. 146.)

rotating with the armature in a cup of mercury, with which it is therefore in metallic communication in every position of the disc. The other extremities of the wires are united together, and passing without metallic contact through the spindle upon which the apparatus turns, terminate in a small slip of copper with two opposite points placed at right angles to the axis. These, in the act of rotation, alternately dip into, and rise above, the mercury in another cup, which may be connected with the first at pleasure by means of a copper wire. By the laws of magnetic induction, the armature becomes a temporary magnet whenever its bent ends are opposite the poles of the magnet, and ceases to be magnetic when they are at right angles to them. The momentary generation and destruction of the magnetic force, which will be oppositely directed in the bar as its opposite ends become opposed to the same poles in the act of rotation, must, by the laws of magneto-electric induction, induce corresponding opposite electric currents in the copper wire if the circuit be complete, by the immersion of the points at the moment of their passage. The points are so arranged, that, standing nearly at right angles to the revolving bar, they just rise from the mercury as its ends become opposed to the poles of the magnet, and the circuit being thus suddenly broken at the moment of the electric wave, the current passes in the form of a brilliant spark.

"This figure represents a section of Mr. Saxton's magneto-electrical machine. *A B* is the horse-shoe magnet. *C D* the armature of soft iron, standing in a transverse direction to the poles of the magnet. *E F* is the spindle upon which it revolves by means of the multiplying wheels, *E G*. *h i* are the metallic wheel and points by which connexion is made and broken between the mercury cup, *K*, and the ends of the coils of wire round the armature, *C D*.



"By means of this magneto-electrical machine, all the well-known effects of voltaic currents may be very commodiously produced. When

the communication is made between the spindle and the revolving disc by means of a fine platinum wire instead of the dipping points, the wire may be maintained at a red heat; although the effect being produced by alternating currents in opposite directions, a kind of pulsation, or intermission of the light, may be discerned. Upon making the communication between the two mercury cups by means of copper cylinders grasped in the hands, a continued painful contraction of the muscles of the arms takes place, which destroys voluntary motion, and, under certain circumstances, is perfectly intolerable. If the currents be transmitted into liquid electrolytes by means of platinum electrodes, they are readily decomposed; but in consequence of the alternate reversal of their direction, the *anions* and *cations* are mixed together. This, however, may be avoided, by turning up one of the points of the axis, when one of the currents will be cut off, and half the power destroyed, but the usual results of polar decomposition will be obtained. The amount of decomposition in this, as in all other cases, is in proportion to the quantity of electricity which circulates. By means of an electro-magnet and a constant battery, which was capable of decomposing water by the primary current at the rate of eleven cubic inches of the mixed gases per minute, four cubic inches have been obtained in the same time by this secondary force."

From the manner in which a magnet in motion induces an electric current, it was presumed that the earth's magnetism might be rendered subservient to the same purpose, and Mr. Faraday found that a soft iron cylinder, introduced into the helix, as above described, and placed in the direction of the dipping needle, occasioned a deviation in the galvanometer; he even found that in a wire, or helix, moved at right angles to the dipping needle, so as to cut the magnetic curves of the earth, an electric current, sensible to the galvanometer, was induced; and that the rotation of a copper globe, or of a plate placed at right angles to the dip, produced the same effect; hence he concludes that the conducting matters of the earth's crust may be similarly affected by its diurnal revolutions, so as to induce electric currents flowing towards the poles, and suggests the possibility of the production of the Aurora, by returning electric currents from the poles into the atmosphere.

I must here bring to a conclusion this brief outline of electricity, and of the extraordinary phenomena arising out of it, such as the attractions and repulsions of masses of matter, chemical affinity, heat, light, and magnetism: how these attributes of matter are connected, or what is the true nature of their mutual dependence, are questions for future decision, when probably the whole subject will be simplified by referring them to one ultimate cause, in which it is not improbable that even gravitation may itself be included. From what has already been attained in this branch of science, some anticipations may be fairly formed of its probable progress hereafter; and if, among these, we admit the possibility of a more unlimited command than we at present possess over the production or extrication of this extraordinary agent, our speculations would assume a very extensive and interesting aspect; its mechanical and chemical powers would be perpetually called into action; the former as a substitute for steam, wind, and water; and the latter for the more sluggish or circuitous and difficult methods of ordinary decomposition; its

single application to the evolution of oxygen and hydrogen from water, would alone work wonders; and even as a direct source of heat and light, its applications and uses would be gigantic and endless; whilst the facility of its conveyance and transmission, its ubiquity, and its varied attributes in those different states which we, for want of more explicit knowledge of their cause, have termed *quantity* and *tension*, seem to point it out as of unlimited application to human uses.

CHAPTER V.

OF SIMPLE SUBSTANCES.

UNDER the term *simple* or *elementary* substances, we include all those bodies which have hitherto resisted decomposition, or resolution into simpler forms of matter; and although it may be presumed that some, or perhaps many of them, are in reality compounds, and that they will be proved to be so, as science advances, and our means of investigation are extended and improved, yet in the present state of our knowledge, in which experiment and not hypothesis is resorted to as the ultimate test, these substances, numerous and varied as they are, have afforded no satisfactory indications of their compound nature, and must, therefore, be considered not as undecomposable but as *undecomposed*. These substances, amounting to fifty-five in number, are alphabetically enumerated in the following table, and their *equivalents* and the abbreviations, or *symbols* by which they are represented in this work, are annexed.

SIMPLE SUBSTANCES.

	Equiv.	Symbol.		Equiv.	Symbol.
1. Aluminium . . .	26	<i>al.</i>	29. Mercury . . .	200	<i>hg.</i>
2. Antimony . . .	65	<i>anst Sb</i>	30. Molybdenum . . .	48	<i>mol.</i>
3. Arsenic . . .	38	<i>ar^{as} As</i>	31. Nickel . . .	28	<i>nie^{Ni} Ni</i>
4. Barium . . .	69	<i>ba.</i>	32. Nitrogen . . .	14	<i>n.</i>
5. Bismuth . . .	72	<i>bi.</i>	33. Osmium . . .	100	<i>os.</i>
6. Boron . . .	11	<i>bo^B B</i>	34. Oxygen . . .	8	<i>o.</i>
7. Bromine . . .	78	<i>br^B Br</i>	35. Palladium . . .	54	<i>pal.</i>
8. Cadmium . . .	56	<i>cad^{cd} Cd</i>	36. Phosphorus . . .	16	<i>p.</i>
9. Calcium . . .	20	<i>cal^h Ca</i>	37. Platinum . . .	99	<i>pla^{pt} Pt</i>
10. Carbon . . .	6	<i>car^C C</i>	38. Potassium . . .	40	<i>po^K K</i>
11. Cerium . . .	48	<i>ce.</i>	39. Rhodium . . .	52	<i>rh.</i>
12. Chlorine . . .	36	<i>cl^{Cl} Cl</i>	40. Selenium . . .	40	<i>se.</i>
13. Chromium . . .	28	<i>chr^{Cr} Cr</i>	41. Silicium . . .	8	<i>si.</i>
14. Cobalt . . .	30	<i>co^b Co</i>	42. Silver . . .	108	<i>ag.</i>
15. Columbium . . .	185	<i>col.</i>	43. Sodium . . .	24	<i>so^{Na} Na</i>
16. Copper . . .	32	<i>cu.</i>	44. Strontium . . .	44	<i>str^{Sr} Sr</i>
17. Fluorine . . .	18	<i>f.</i>	45. Sulphur . . .	16	<i>s.</i>
18. Glucinum . . .	18	<i>gl.</i>	46. Tellurium . . .	32	<i>tel.</i>
19. Gold . . .	200	<i>au.</i>	47. Thorium . . .	60	<i>th.</i>
20. Hydrogen . . .	1	<i>h.</i>	48. Tin . . .	58	<i>sta^{Sn} Sn</i>
21. Iodine . . .	126	<i>i.</i>	49. Titanium . . .	24	<i>ti.</i>
22. Iridium . . .	96	<i>ir.</i>	50. Tungsten . . .	100	<i>tu.</i>
23. Iron . . .	28	<i>fe.</i>	51. Vanadium . . .	68	<i>va.</i>
24. Lanthanum . . .		<i>lan.</i>	52. Uranium . . .	217	<i>ur^{um} U</i>
25. Lead . . .	104	<i>pl^{Pb} Pb</i>	53. Yttrium . . .	2	<i>yt.</i>
26. Lithium . . .	8	<i>li.</i>	54. Zinc . . .	32	<i>zn.</i>
27. Magnesium . . .	12	<i>mag^{Mg} Mg</i>	55. Zirconium . . .	22	<i>zir.</i>
28. Manganese . . .	28	<i>man^{Mn} Mn</i>			

The preceding list admits of an easy, obvious, and useful division, into *substances which are, and which are not metallic*, and there are general analogies among the *metals* which enable us to subdivide them into classes; but with respect to the *non-metallic* bodies, the subdivision is more difficult, and the principles of classification usually applied to them are, in many respects, objectionable. If their arrangement be founded either upon their general electrical or chemical relations, as, for instance, into *electro-negative* and *electro-positive* bodies (anions and cations), or into *supporters of combustion* and *combustibles*, or into *acidifying* and *acidifiable* substances, difficulties occur in the details, which are of great practical inconvenience; for the electrical arrangement brings together substances extremely dissimilar in their chemical characters, such, for instance, as oxygen and sulphur, both of which are electro-negative bodies, or *anions*; and the chemical arrangement leads us at one time to class oxygen with sulphur, both being supporters of combustion; and at another to separate them, in consequence of oxygen being eminently a supporter of combustion, and sulphur as eminently a combustible. Again, in regard to the terms *acidifying* and *acidifiable*; oxygen and chlorine are included among the former, and hydrogen and sulphur among the latter; yet oxygen and chlorine combine with each other to form acids, and neither of them being, in any sense of the term, *combustible*, it is difficult to say which is the acidifying and which the acidifiable element: the compound of hydrogen and sulphur is also acid, yet both hydrogen and sulphur are *combustible*, and hydrogen is *acidifiable* in respect to chlorine, as sulphur is in respect to oxygen. In all these arrangements, too, nitrogen stands out (regarding it as elementary), as an obstinate exception; it is *acidifiable* by oxygen, but it is *alkalifiable* by hydrogen; it is neither *combustible*, nor is it in any case a *supporter of combustion*; and its electro-chemical relations are doubtful: indeed the distinction between some of these bodies and the *metals* is not in all cases very definite: there are strong analogies between arsenic, and selenium, and sulphur, so that Berzelius actually arranges selenium with the metals; and some forms of carbon approach so closely in their characters to those of a metal, that Döbereiner speaks of *carbonium* as a metal. Under all these difficulties, many writers have rejected the electrical and chemical analogies of the unmetallic elements as the basis of their classification, and have arranged them, in reference to their supposed importance as chemical agents, and to convenience of discussion: Berzelius divides them, generally, into *oxygen*, which he places by itself as a supporter of combustion, and into *inflammable substances*, in which he includes all the other elements; and then, adverting particularly to the *unmetallic* substances, he subdivides them into three classes, namely,—1. *Permanently elastic or gaseous bodies* (*Gazolyta*): oxygen, hydrogen, nitrogen. 2ndly. *Metalloids*: sulphur, phosphorus, carbon, boron, and silicon. 3rdly. *Salifying substances*, (*Halogenia*): chlorine, fluorine, iodine, bromine. Almost all agree in placing *oxygen* at the head of the list; but scarcely any systematic writers concur in the order in which they describe the remaining unmetallic elements; except, indeed, that they usually place *hydrogen* after oxygen. But the most important difference amongst them is, in what relates to the *compound substances*, some describing them along with, or immediately

after, their respective elements: and others giving the abstract history of each element separately, and then referring to their mutual combinations. It would be useless to point out in detail the objections which may be made to each systematic arrangement, for, after all, that will be preferable which is best calculated to guide and assist the student in the acquisition of the leading facts and doctrines of the science, and which is, at the same time, most convenient for reference. Under these circumstances I have retained, with such modifications as the progress of chemistry has rendered necessary, the general plan adopted in the former editions of this work. Oxygen, and the bodies associated with it in many of their electrical and chemical habitudes, stand first on the list (the *Halogenia* of Berzelius); and these are succeeded by the inflammable and acidifiable bases; but I have not thought it advisable, for reasons just mentioned, to divide them, as formerly, into two classes: they will be described, therefore, in the following order:

1. OXYGEN.
2. CHLORINE, and its combinations with oxygen.
3. IODINE, and its combinations with oxygen and chlorine.
4. BROMINE, and its combinations with the three preceding substances.
5. FLUORINE, and its combinations with the four preceding substances.
6. HYDROGEN, and its combinations with the five preceding substances.
7. NITROGEN, and its combinations with the six preceding substances.
8. SULPHUR, and its combinations with the seven preceding substances.
9. SELENIUM, and its combinations with the eight preceding substances.
10. PHOSPHORUS, and its combinations with the nine preceding substances.
11. CARBON, and its combinations with the ten preceding substances.
12. BORON, and its combinations with the eleven preceding substances.

Arranging these substances according to their analogies, as pointed out by Berzelius, they would stand as follows, but such arrangement, if here adopted, would, I think, be less convenient in its details than that which I have proposed.

GAZOLYTES.

Oxygen.
Hydrogen.
Nitrogen.

HALOGENS.

Chlorine.
Iodine.
Bromine.
Fluorine.

METALLOIDS.

Sulphur.
Selenium.
Phosphorus.
Carbon.
Boron.
Silicon*.

I have not here separately enumerated the *compounds*, as they will be found in the *table of contents*, by reference to which it will also be seen that the same general plan is adopted in respect to the *metals*, the principle on which they are classified being stated in the preliminary observations on their general properties.

The origin of the *names* by which the simple substances are distinguished, will be found under their individual history, but it will be neces-

* I have retained *Silicon*, or *Silicium*, among the *metals* for the convenience which such arrangement affords in describing some of its most important compounds, such as glass, artificial gems, and coloured glasses, in which the metals and their oxides are so essentially concerned.

sary here to advert to the general principles of *nomenclature* applied to their mutual combinations.

All the combinations of oxygen, chlorine, iodine, bromine, and fluorine, with the inflammables and the metals which are *not acid*, are called *oxides, chlorides, iodides, bromides, and fluorides*: the combinations of the inflammable substances with each other, and with the metals, are distinguished by the termination *uret*, as *sulphuret, phosphuret, &c.*, and in some cases the combinations of certain metals with each other are similarly designated: thus we speak of *arseniurets, tellurets, and antimoniuurets*.

The different *proportions* of oxygen in the oxides are distinguished by a prefix derived from the Latin or Greek numerals; thus we have *protoxide, deutoxide* or *binoxide, tritoxide* or *teroxide*, for the first, second, and third stages of oxidizement; and the highest degree of oxidizement is termed *peroxide*; when the proportions of oxygen in an oxide are as 1 to $1\frac{1}{2}$, or intermediate between the protoxide and deutoxide, the compound is termed a *sesqui-oxide*. If the oxide is so constituted as to contain 2 atoms of base, and 1 of oxygen, it is then termed a *suboxide*, or, more definitely, a *dioxide*. The same distinctive nomenclature is applied to the chlorides, iodides, sulphurets, phosphurets, &c.

The names of the *acid* compounds of oxygen are derived from their bases, and where there is only *one*, it is usually designated by the termination *ic*, as *Carbonic acid, Boric acid, Cyanic acid, &c.*; where there are *two* acids of the same base and oxygen, that containing the smallest proportion of oxygen is distinguished by the termination *ous*, and that containing the larger proportion by the termination *ic*; as *arsenious* and *arsenic acid*: where there are *more than two* acid compounds of the same base, more complicated terms are requisite, of which the nomenclature of the acids of sulphur forms a good example; these are *four* in number, and are termed—1. *hyposulphurous acid*; 2. *sulphurous acid*; 3. *hyposulphuric acid*; 4. *sulphuric acid*; and occasionally the acid containing the *maximum* of oxygen is further distinguished by the prefix *per* or *oxy*: thus we sometimes use the terms *oxychloric acid, permanganic acid, &c.* The *saline* combinations of the acids ending in *ous* are distinguished by the termination *ite*, and of those ending in *ic*, by the termination *ate*: thus we have a *hyposulphite*, a *sulphite*, a *hyposulphate*, and a *sulphate* of potassa, &c., and where the acid and base unite in more than one proportion, a distinction similar to that applied to the oxides is resorted to; thus the compound of one atom of potassa and *two* of sulphuric acid is a *bisulphate* of potassa: that of *two* atoms of oxide of lead and one of nitric acid, a *dinitrate* of lead: these are also sometimes called *supersulphate* of potassa, and *subnitrate* of lead; but the preceding terms are more definite. Lastly, the same acid occasionally forms distinct compounds with the protoxide and peroxide of the same metal, forming *protosalts* and *persalts*. Thus we have a *protosulphate* and a *persulphate* of iron, &c. Other more complex cases of nomenclature occasionally arise out of the preceding, which, however, will be sufficiently intelligible when they occur, by reference to the context.

CHEMICAL SYMBOLS.—It may now be necessary to say a few words respecting the *symbols* contained in the preceding table, and the *formulae* in which they will occasionally be used. It is obvious that they repre-

sent the *equivalents* or *atoms* of the elements; thus $n+o$ signifies 1 equivalent or atom of nitrogen = 14, and 1 of oxygen = 8, the sign + implying *combination*; or they may be written either in brackets, thus $(n+o)$, or a line is drawn over them, thus, $\overline{n+o}$. The *number* attached to either symbol indicates the number of atoms of either element in the compound; nitric acid, for instance, is a compound of 1 atom of nitrogen, and 5 atoms of oxygen, and is, therefore, thus written $(n+5o)$. Potassa is a compound of single atoms of potassium and oxygen, and is therefore simply represented by $(po+o)$. Sulphuric acid consists of 1 atom of sulphur = 16 in combination with 3 atoms of oxygen $(8 \times 3) = 24$, and is represented by $(s+3o)$. Sulphate of potassa is composed of 1 atom of potassa = 48, and 1 atom of sulphuric acid = 40, and would therefore be written in symbols thus $\overline{(po+o)+(s+3o)}$. In this case the *proximate* elements of the salt are sufficiently distinguished: but if the object were to express merely its *ultimate* elements these would be written $po+s+4o$. A number on the outside of the bracket indicates the number of the atoms or equivalents of the compound within it: thus, bisulphate of potassa, composed of 1 equivalent of potassa and 2 of sulphuric acid, is represented by $(po+o)+^2(s+3o)$. In regard to water, the salifiable oxides, and the acids, it is often convenient to have symbols representing the *compound*, without reference to its elements, and I shall accordingly, for this purpose, represent the alkalis and salifiable protoxides by capital initials; the common acids by an acute accent over the initial of the base; the peracids by two acute accents; and the subacids by a grave accent; the latter with the addition of a line underneath may indicate the hypoacids. Water may be represented by the letter *q*, from *aqua*. The following table shows a few of the applications of these *abbreviations*, or compound symbols, as opposed to the more circuitous instances of elementary symbols.

	Atomic Symbol.	Abbreviation.
Water	$(h+o)$	<i>q</i>
Potassa	$(po+o)$	P
Soda	$(so+o)$	S
Baryta	$(ba+o)$	B
Oxide of Lead	$(pl+o)$	PL
Hyposulphurous Acid	$(2s+2o)$	$\underset{\sim}{s}$
Sulphurous Acid	$(s+2o)$	\bar{s}
Hyposulphuric Acid	$(2s+5o)$	$\underset{\sim}{s}'$
Sulphuric Acid	$(s+3o)$	\bar{s}'
Sulphate of Potassa	$\overline{(s+3o)+(po+o)}$	$(s'+P)$
Hydrated Potassa	$\overline{(po+o)+(h+o)}$	$(P+q)$
Nitrate of Lead	$\overline{(n+5o)+(pl+o)}$	$(n'+PL)$
Carbonate of Ammonia	$\overline{(car+2o)+(n+3h)}$	$(car'+A)$

In these and the preceding symbols, I have availed myself, with some slight changes, of the principles suggested by Mr. Whewell,

(*Journal of Royal Institution*, I., 437). The symbols of the *elementary substances*, used by Berzelius, differ but little from those which I have adopted, and I have followed him in employing the initial letters of their ordinary Latin names: with this difference only, that he represents potassium, sodium, and antimony, by the initials K. Na. and Sb. (kalium, natrium, and stibium), instead of *po*, *so*, and *an*. In other respects, however, I have found it necessary to introduce some deviations, or rather to reject parts of his method. Berzelius indicates the *atoms* of oxygen by dots placed over the symbol; thus, instead of writing $(n + 50)$ for *nitric*

acid, he uses the abbreviation $\overset{\cdot\cdot\cdot}{\text{N}}$. In like manner he denotes the compounds of *sulphur* by commas; thus, *sulphuretted hydrogen* ($s + h$) he

writes $\overset{2}{\text{H}}$; and where he wishes to represent *two* equivalents of an element, they are denoted by a *dash through* or *under* its symbol; thus $\overset{\text{H}}{\text{H}}$ or $\underset{\text{H}}{\text{H}}$, indicates 2 atoms of hydrogen. The *vegetable* and *animal acids* he abbreviates by using the first letter of their name with a dash *over* it, thus $\overset{\text{T}}{\text{C}}$ $\overset{\text{T}}{\text{C}}$ $\overset{\text{T}}{\text{F}}$ are the *tartaric*, *citric*, and *formic acids*. He also often omits the sign +, and writes the combined elements side by side, the sign of

addition being understood: thus he writes nitrate of baryta, $\text{Ba } \overset{\cdot\cdot\cdot}{\text{N}}$

instead of $\text{Ba} + \overset{\cdot\cdot\cdot}{\text{N}}$. Lastly, he denotes two or more equivalents of one constituent of a compound, by numbers placed in the same position as the indices of powers in Algebra; thus $\text{N } \overset{\cdot\cdot\cdot}{\text{H}}^3$ is the same as $(n + 3h)$. My chief reason for modifying these abbreviations in the way which I have above proposed, is to avoid the obscurity in which they are frequently involved, and the facility with which they become perplexed by imperfect printing, or errors of the press. It must, however, be confessed that in many cases, the representation of the atoms of oxygen by dots above the basic symbol is convenient.

It may perhaps be objected to the abbreviated symbols which I have suggested that they do not carry with them explicit indications of atomic composition: that *nitric acid* for instance is more completely represented

by $\overset{\cdot\cdot\cdot}{\text{N}}$ than by n' , and phosphoric acid by $\overset{\cdot\cdot\cdot}{\text{P}}$ than by p' , but this can only affect the casual reader, and for such, the system of symbols is scarcely profitable in any form.

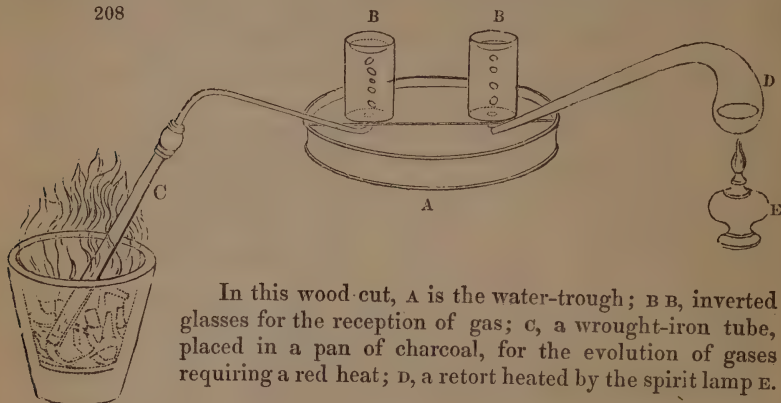
The great use of symbols is visibly as it were to present the elements of compounds, so that all their possible combinations may be traced with comparative facility, and their less obvious relations detected. They also facilitate the complex computations required in reference to the atomic constitution of various organic compounds, and often enable the teacher to present the student, at one view, with details which, in the ordinary mode of proceeding, would be verbose and complex. Thus the conversion by heat of 1 atom of nitrate of ammonia into 2 of protoxide of nitrogen, and 3 of water, is thus concisely represented:

Nitric Acid.	Ammonia.	Nitrous protoxide.	Water.
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$(n + 50) + (n + 3h)$ produce $2(n + 0)$ and $3(h + 0)$: or, taking the ultimate elements of nitrate of ammonia as $2n + 50 + 3h$, they form $2(n + 0) + 3q$: and of such applications many instances will afterwards occur.

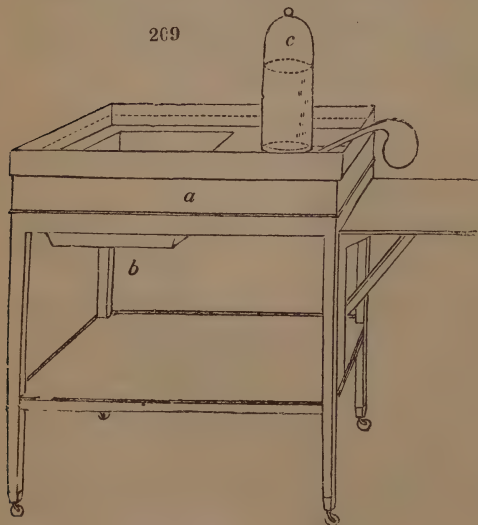
PNEUMATIC APPARATUS.—Of the simple substances which we are about to examine, four are known to us in the gaseous state, and amongst their combinations there are many which also assume that form; so that it will be necessary before we enter upon their history, to say a few words respecting the apparatus by which gaseous bodies are procured and examined. The *hydro-pneumatic apparatus* consists of a japanned iron or copper vessel, of different shape and size according to the particular purposes for which it is intended, and containing a shelf perforated with holes through which the gas may pass into inverted vessels properly placed for its reception.

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In this wood cut, A is the water-trough; B B, inverted glasses for the reception of gas; C, a wrought-iron tube, placed in a pan of charcoal, for the evolution of gases requiring a red heat; D, a retort heated by the spirit lamp E.

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For experiments, in which *large vessels* are employed for collecting or transferring gases, the annexed form of the apparatus (fig. 209) is most convenient: the trough is placed in a wooden frame or stand *a*; it has a deep part at *b*, and a shallow shelf, upon which the inverted jar may be placed over a groove, as at *c*.

Vessels of various forms are employed for receiving, retaining, and measuring gases. Where it is intended to introduce different substances into the gas, they may be of

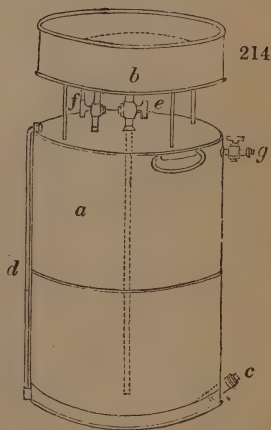
the form represented in figure 209, drawn into a neck with a glass-stopper at top, and open at bottom. Some of these should be graduated into cubic inches, and supplied with a stop-cock, as in figure 211. For measuring small quantities of gases, tubes are employed, some of which

should be divided into 100 equal parts, others into tenths and hundredths of a cubical inch, as in figures 212 and 213.



Where large quantities of gases are required to be collected and preserved, we employ *gasholders* and *gasometers*. The annexed cut (fig. 214) represents Mr. Pepys's improved gasholder, made of japanned iron, or what is preferable, of copper. It consists of a body or reservoir *a*, which may hold from two to six or eight gallons:

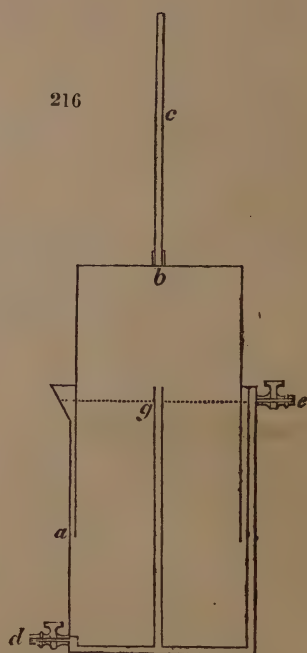
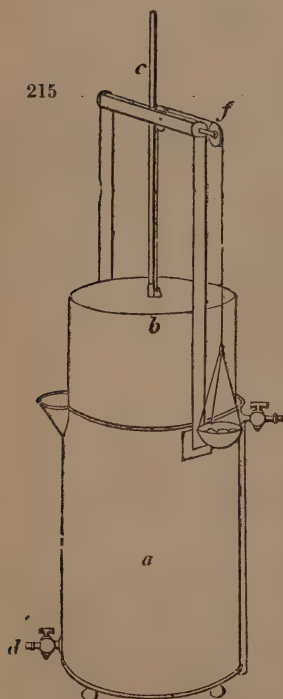
b, is a cistern from which issue two tubes, supplied with stop-cocks, one entering the reservoir at its upper part, the other continued, as shown by the dotted lines, to near the bottom: *c*, is a short tube issuing from the bottom of the reservoir, and capable of being accurately closed by a screw. *d*, is a glass tube communicating at both ends with the body of the gasholder. When it is intended to fill this apparatus with gas, the tube *c* is closed, and the stop-cocks, *e*, *f*, are opened; water is then poured into the cistern, which, running down the long tube *e*, forces the air out through the shorter one *f*. The reservoir being thus filled, the stop-cocks are closed, and the aperture *c* is opened, into which



the beak of the retort, or tube, whence the gas issues, is introduced, and, bubbling up, displaces the water which runs out at the same opening. When it is seen in the tube, *d*, that nearly the whole of the water is displaced, the aperture *c* is closed; the vessel is now filled with gas, which may either be drawn off into receivers, placed in the cistern *b*, by opening the two stop-cocks *e*, *f*; or by closing the stop-cock *f*, and opening *g*, it may be propelled into bladders, or transferred in any convenient way by an attached tube.

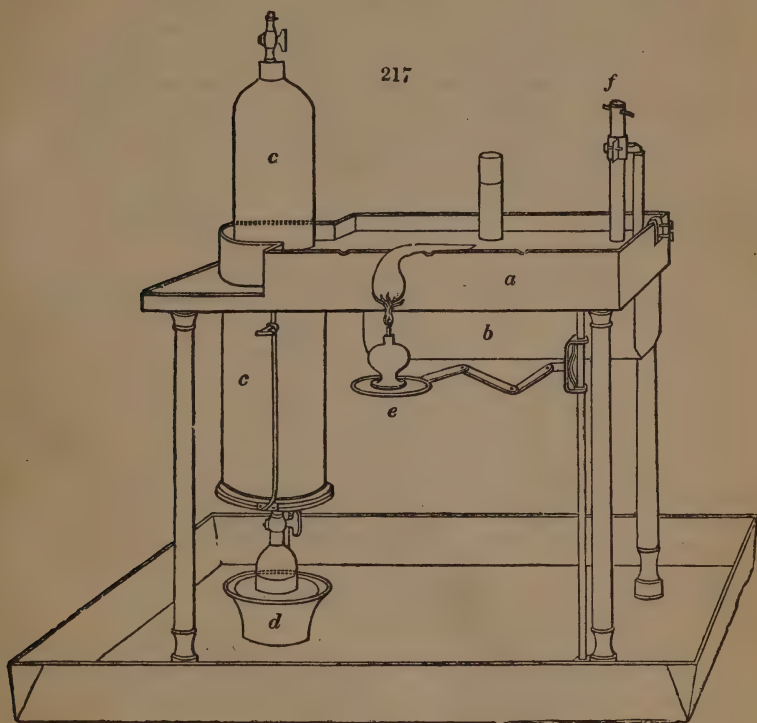
A view and section of the *gasometer* are shown in the following sketches (figs. 215, 216): it may be made of japanned iron or copper. *a a*, is the outer circular vessel, or pail, to the sides of which the tubes *d*, *e*, (each fitted with a stop-cock externally,) are soldered. The tube *d* passes along the

bottom of the pail, and proceeds to the centre, where it joins the tube *e*, which commences at the top of the pail at the cock *e*, and proceeds downwards; and, from the place of junction, the upright tube *g* rises through the middle of the pail, a little above the level of its upper rim. The vessel *b* is a cylinder open only at the bottom, and of less diameter than the pail in which it is inverted, and can move up and down freely. This cylinder has a solid stem *c*, which passes through a hole in the cross-bar of the frame fixed to the top of the pail; it serves to steady the cylinder, and to indicate the quantity of the enclosed gas; the weight of the cylinder is counterpoised in any convenient way; generally by a weight and chord passing over the pulley *f*.



To use this gasometer, first let the cylinder fall to the bottom of the pail, and fill the latter with water; then shut the cock *e*, and open *d*, and connect with it the tube which conveys the gas from the retort, gasholder, or other vessel; or, if more convenient, shut *d*, and convey the gas through *e*. The gas rises, and gradually lifts up the cylinder, which must be properly balanced: and when sufficiently filled, the cock, by which it entered, must be closed. The gas may now be drawn off at either of the stop-cocks, by a tube passing into the water-trough, or it may be propelled through a blow-pipe, or otherwise employed.

Those gases which are absorbed by water, may, in most instances, be collected over mercury. The best form of the *Mercurio-pneumatic apparatus* is that contrived by Newman (*Quarterly Journal*, vol. i., p. 185). It is a trough of cast-iron, supported by brass or iron legs, and having a small gasometer at one end. It is placed in a japanned iron tray to collect the scattered mercury, as shown in the wood-cut (fig. 217).



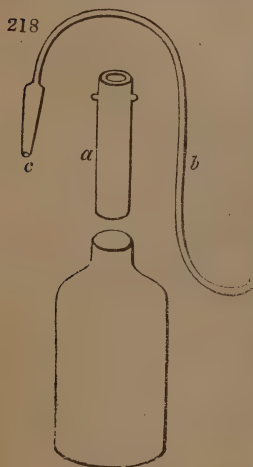
a is the shallow, *b* the deeper part, of the trough; *c* is a small mercurial gasometer connected with it, filled from the bottom through the small basin of mercury at *d*; *e* is a sliding stand for a lamp, *f* a detonating tube, screwed into a spring support. It frequently happens that a mercurial pneumatic trough, upon a much smaller scale than the above, is sufficient for mere experiments of research; and, in that case, it is either made of cast-iron or of wood, being hollowed out of a block of mahogany. The chemical lecturer may in many instances altogether dispense with the trouble and expense of a mercurial-bath, by availing himself of the method of collecting gases in dry glass vessels, as described at page 366; especially when he requires very large jars or bottles to be filled with gas, and at the same time kept *dry*, but where a small admixture of atmospheric air is unimportant.

§ I. OXYGEN.

THIS elementary body was discovered by Priestley on the 1st of August, 1774; he called it *dephlogisticated air*; it was termed *empyreal air* by Scheele, and *vital air* by Condorcet. The name *oxygen*, was given to it by the French nomenclaturists, implying its tendency to form *acid* compounds (from $\acute{o}\xi\upsilon\varsigma$, *acid*, and $\gammaεννέιν$, *to generate*). It is more abundantly diffused throughout nature than any of the other elementary bodies; it forms eight-ninths of the weight of water, about one-fifth of the weight of the atmosphere, and a large relative proportion of the mineral bodies which form the solid matter of the globe. It also forms, with scarcely one exception, an element of the various products of organized bodies both animal and vegetable.

Oxygen gas may be procured by a variety of processes, of which those only in common use will be noticed here, and others adverted to in their proper places.

To obtain oxygen in the purest state, proceed as follows: introduce into a small glass *retort* (as shown at D, fig. 208,) about 100 grains of the salt called *chlorate of potassa*, and gradually heat it over a gentle charcoal fire, or by means of a large spirit-lamp, having previously placed the beak of the retort under the shelf of the hydro-pneumatic apparatus. Suffer the common air of the retort to escape, and when the salt fuses and appears to boil, collect the oxygen which it then gives out in proper vessels, taking care so to adjust the heat as to cause the gradual decomposition of the salt, and occasion the air-bubbles to follow each other with moderate rapidity, especially towards the end of the process, when a torrent of gas is apt to be rather suddenly evolved, in consequence of the formation of a portion of perchlorate of potassa, which is decomposed at that period. At last, the heat may be so far increased as to render the bottom of the retort red-hot, being careful, however, not to fuse it; when gas ceases to be evolved, withdraw the retort and put it aside: it is seldom fit for a second operation. From 100 grains of the chlorate, we may expect to obtain nearly 100 cubic inches of gas.



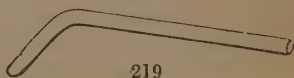
Another substance from which oxygen may be obtained, at a cheaper rate, is *black oxide of manganese*, but the gas is not perfectly pure, and the quantity produced from a given weight of the oxide is very variable. A pound should yield from 40 to 50 pint measures. (11 ounces troy, will give 1 ounce, or 1387 cubic inches. —THOMSON. 1 ounce yields, if quite pure, 128 cubic inches. —TURNER.) The oxide of manganese should be powdered, dried, and introduced into an iron gas bottle, which may be about four-fifths filled with it, and placed with its proper connecting tubes, in a convenient furnace or fire-place. These bottles should be made of wrought-iron, of the shape annexed (fig. 218), their capacity being from one to three pints. The connecting tube *a* should

be of iron, and fitted by grinding into the neck of the bottle; and the delivery tube *b*, which may be of pewter, with a brass or copper piece soldered on to it at its conical end *c*, should be similarly ground into the upper end of the connector. When these bottles are used, the joints may be made tight by the previous application of a little grease.

When the oxide of manganese becomes red-hot, the oxygen begins to escape by the pewter tube, which must be so bent as to pass under the shelf of the water apparatus. Collect some of the gas in a small jar or tube, and test it by introducing into it a slip of wood which has been inflamed and blown out, so that the end remains only glowing; if the gas be sufficiently pure, it will immediately burst into flame and burn vehemently: the oxygen may then be collected for use, either in bottles, jars, gasholders, or gasometers, as required. When the gas ceases to be evolved, the bottle must be removed from the fire; and, when cold, emptied of its contents, which will be found to be an oxide of manganese, of a brown colour, containing of course less oxygen than the black, and not further decomposable by heat alone.

Oxygen gas may also be obtained from a mixture of pulverised black oxide of manganese and sulphuric acid, in such proportions as to be about the thickness of cream; this mixture is put into a glass retort, and heated over an Argand lamp, the gas being collected in the usual way. This method is sometimes convenient where an iron retort cannot be procured; but it is not economical, and the ingredients are apt to harden in the retort, which is often broken in attempting to cleanse it.

If perfectly pure oxygen be required, it must not only be obtained from chlorate of potassa, but also collected over mercury; and as it is often wanted in the experimental laboratory in very small quantities only, a tube-retort, made of green or plate-glass, bent into the annexed form (fig. 219), may be conveniently used.



It must also be recollected, in all delicate experiments with oxygen and other gases, that they retain, as usually procured, more or less vapour of water, so that to obtain them *dry*, it is necessary to convey them through tubes over substances which will abstract the watery vapour which they contain, without in any way affecting the purity of the gas itself. Oxygen may thus be dried by passing it through a long tube containing fragments of fused *chloride of calcium*: sulphuric acid, fused potassa, and some other substances, are occasionally used for the same purpose.

Oxygen gas is insipid, colourless, and inodorous; it is permanently elastic, under all known pressures and temperatures. Its specific gravity, compared with air, is as 1.111 to 1.000. Compared with hydrogen, its specific gravity is = 16, hydrogen being = 1. At mean temperature and pressure, 100 cubic inches weigh 34.60 grains: or according to Thomson, 36.43 grains at the temperature of 32°. According to Dulong and Berzelius, the specific gravity of oxygen is 1.1026, and 100 cubic inches weigh 34.109 grains (*Ann. de Chim. et Phys.*, xv., 386); according to Davy, its specific gravity is 1.127. Its refractive power, in regard to light, is less than that of any known body: compared in this respect with

atmospheric air, it is as 0·830 to 1000. According to De la Roche and Berard, its specific heat, compared with an equal *volume* of air, is = 0·9765, and with an equal *weight* of air, = 0·8848, that of air being = 1·000. It is evolved by electrolytic action at the positive pole or anode, and therefore stands among the anions, as defined by Faraday, (p. 307: and figs. 163 and 164.)

When powerfully compressed by the sudden depression of a piston in a glass tube, oxygen appears to become momentarily luminous, a property which has been considered as one of its characteristics. Thenard, however, has shown that this appearance is connected with the presence of grease or oil upon the compressing piston, and that the gas, although much heated by sudden compression, is not of itself luminous. It is absorbed in very small quantity only by water: 100 cubic inches of water, freed from air, only taking up 3·5 cubic inches of oxygen (HENRY, *Phil. Trans.*, 1804, p. 174). It does not alter the colour of litmus, nor does it render lime-water turbid.

It is a powerful supporter of respiration. A small animal, confined in oxygen gas, lives thrice as long as when confined in the same bulk of common air; it has, therefore, been called *vital air*; but we are not thence to conclude that it is fit for the continuous support of life: on the contrary, an animal made to breathe oxygen for any length of time, falls a sacrifice to excess of arterial action, and after death the blood in the veins is found as florid as that in the arteries.

Oxygen eminently *supports combustion*. A lighted taper, introduced into this gas, is very rapidly consumed, with intense ignition and enlargement of the flame; and if it be previously blown out, so that the wick continues glowing (and for such experiments pieces of *green wax*-taper answer best), it immediately bursts into flame when plunged into the jar of oxygen. Sulphur, which burns in the air with a small blue flame, has its flame enlarged when immersed in a jar of oxygen, and blazes with a beautiful purple colour. It dissolves as it were in the oxygen, and converts it into sulphurous acid gas, which is absorbed by water. Phosphorus, when inflamed in the atmosphere, burns with a bright light, but in oxygen the eye can scarcely bear its brilliancy, and the heat which it evolves is very intense. A piece not larger than a pea should be used in the experiment. The oxygen combines with the phosphorus, and forms a quantity of white flaky matter, very soluble and deliquescent, which is chiefly phosphoric acid. This, and the combustion of sulphur, may be best performed by placing them in a small copper spoon or cup, attached to a wire annexed to a spare stopper, or passing through a cork which fits the neck of the air-jar. The disadvantage of a cork is, that it is sometimes apt itself to take fire and crack the jar.

One of the most brilliant instances of combustion in oxygen is the burning of iron wire. For this purpose the jar should be capacious, and placed over water in a common soup-plate; the oxygen should be very pure. A piece of thickish annealed iron-wire should be attached to the spare stopper, and loosely wound round with repeated twists of harpsichord-wire, so as to form a tangled coil, nearly the thickness of one's finger; the sulphur tip of a match should then be broken off, and affixed to the end of it; when this is inflamed, and the coil immersed into the

jar of gas, vivid combustion soon ensues: it throws off brilliant sparks, and partly fuses into globules of oxide iron, which fall through the water, and lie for some time red-hot upon the plate, which they often fuse at the point of contact. A piece of annealed watch-spring, a thin file, or long shavings which may be obtained from the turners of steel or iron, may also be used for this experiment.

In all these cases of combustion in oxygen gas, the sudden expansions which take place are apt to endanger the bell-glass, which should, therefore, be held by the hand, so as to allow the occasional escape of a little of the gas, and at the same time prevent its jarring upon the plate beneath.

The results of the above, and other cases of combustion in oxygen, will be more fully detailed and explained hereafter.—(See CARBON, SULPHUR, PHOSPHORUS, and IRON.) It may suffice to state at present, that in all cases of combustion in oxygen, the combustible and the oxygen combine, and the product of combustion consequently manifests an increase in weight proportionate to the quantity of oxygen with which it has united. *Acids, alkalis, earths, and oxides*, will be found to be the result of these combinations, which are either effected slowly, and without the evolution of heat and light; or rapidly, with the phenomena of combustion and flame: or with intermediate rapidity, exciting considerable elevation of temperature, and often even a red heat, though without flame, as in some cases which have been already cited (p. 225).

The terms *oxidizement* and *oxidation* imply the combination of oxygen with bodies; and its abstraction or separation is *deoxidizement* or *reduction*. All the elementary substances are susceptible of oxidizement, and most of them, at certain temperatures, with the evolution of heat and light; these are in common language termed *combustible*, or *inflammable bodies*; when a substance is saturated with oxygen, it becomes *incombustible*; that is, incapable of entering into further combination with it. Bodies saturated with the other supporters of combustion are also incombustible, hence the perchlorides, periodides, &c., come usually under that definition. All *organic* bodies are combustible.

The *phenomena of combustion* were referred by Stahl and his associates to a peculiar principle which they called *phlogiston*; it was supposed to exist in all combustibles, and combustion was said to depend upon its separation: but this explanation, though apparently supported by experimental evidence, was at variance with the well-known fact, that bodies during combustion increase in weight.—See *History of Chemistry*, p. 35.

After the discovery of oxygen gas, it was adopted by Lavoisier as the universal supporter of combustion. The basis of the gas was supposed to unite to the combustible, and the heat and light which it before contained in the gaseous state, were said to be evolved in the form of flame. But in this hypothesis several requisites are not fulfilled; the light depends upon the combustible, and not upon the quantity of oxygen consumed; and there are numerous instances of combustion in which oxygen, instead of being solidified, becomes gaseous during the operation, so that the theory of latent heat is insufficient; and, lastly, in others, no oxygen whatever is present. Combustion, therefore, cannot be regarded as dependent upon any peculiar principle or form of matter, but must be considered as a general result of intense chemical action. It may be

connected with the electrical energies of bodies; for all bodies which powerfully act upon each other are in the opposite electrical states of positive and negative; and the evolution of heat and light may depend upon the annihilation of these opposite states, which happens whenever they combine.—See the *Prefatory History of Chemistry*; the Section on *Electricity*; and the article *Atmospheric Air*.

§ II. CHLORINE.

CHLORINE was discovered by Scheele in 1774. Consistently with his theoretical notions of its nature, he called it *dephlogisticated muriatic acid*.—(*Mem. Acad. Stockholm*, 1774, p. 94.) The term *oxymuriatic acid* was afterwards applied to it by the French chemists.—(BERTHOLLET, *Jour. de Phys.*, p. 325.) The more appropriate term *chlorine*, (from *χλωρὸς*, *green*;) which merely designates its greenish-yellow colour, was given to it by Sir H. Davy, who, in 1810, published a masterly essay on its nature, in the *Phil. Trans.*, showing that, so far from containing loosely-combined oxygen, as had been suspected, that element could not be proved to exist as one of its component parts; also that it contained no muriatic acid; that in all cases of the *apparent* evolution of oxygen and muriatic acid from chlorine, water was present, and was decomposed; and that, in the present state of our knowledge, chlorine must be regarded as an uncompounded or elementary body. Its great natural source is sea-salt, or *chloride of sodium*: it also occurs in several other combinations.

To obtain chlorine, a mixture of one part by weight of coarsely-powdered black oxide of manganese and two parts of common hydrochloric acid may be heated over a lamp in a glass retort. Chlorine is soon copiously evolved, and may be conveniently collected over warm water; it is absorbed by cold water, and cannot, therefore, be long retained over that fluid; so that it should be received into bottles provided with ground stoppers: when these are full, the stopper, previously greased a little, should be introduced under water, care being taken to exclude the water from their interiors. In consequence of the deleterious nature of chlorine, its escape into the atmosphere of the laboratory should be prevented, by collecting the first portions which come over mixed with the common air of the retort, in a jar, which may afterwards be carried away into the open air, or placed under a chimney. The gas may be preserved for use when it passes over of its full colour, to judge of which, the neck of the retort should be kept clean; it should not be more than half filled with the materials, which are otherwise apt to boil over, and soil the water in the trough.

When chlorine is required perfectly pure and free from hygrometric moisture, it should be first passed through water, and afterwards conducted through a long tube containing fragments of fused chloride of calcium, and ultimately into a clean dry bottle, from which it will expel the atmospheric air, as explained by fig. 222; it cannot be collected over mercury, as it immediately combines with that metal.

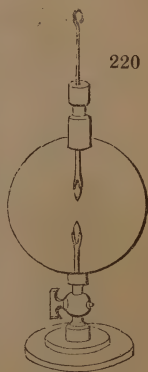
Chlorine may also be procured from a mixture of 8 parts of common salt, 3 of pulverized black oxide of manganese, 4 of water, and 5 of sulphuric acid: or the proportions recommended by Thenard may be used; viz., 4 parts of common salt, 1 part of oxide of manganese, 2 of

sulphuric acid, and 2 of water. The theory of its production in these cases will be explained afterwards.—See *Hydrochloric Acid*, and *Sulphate of Soda*.

Chlorine, at common temperatures and pressures, is a gaseous fluid, which, when perfectly dry, suffers no change by exposure to a temperature much below 0° ; but, in its ordinary state, it generally contains aqueous vapour, which, at a temperature of 32° , is deposited in combination with chlorine in the form of a white crystalline compound, which liquifies, effervesces, and is again taken up by the gas, upon the application of heat. This *hydrate of chlorine* may be best obtained by introducing into a clean bottle of the gas a little water, and keeping it for a few days in a dark place, at a temperature not exceeding 32° . It then forms prismatic and acicular crystals, having a specific gravity of about 1.2 and composed, according to Faraday, of 27.7 chlorine and 72.3 water, or about 1 proportional of chlorine to 10 of water.—(*Quarterly Journal*, xv.) Chlorine was the first of the gases supposed to be permanently elastic which Mr. Faraday succeeded in condensing into the liquid state: he effected this by putting some of the hydrate of chlorine into a small bent tube, hermetically sealed, and applying a gentle heat, a yellow vapour formed, which condensed in the cold part of the tube into two distinct fluids, the uppermost and lightest of which was mere aqueous solution of chlorine, but the heavier was yellow, and separable by careful distillation; it did not solidify at 0° . If, when the fluids were separated, the tube was cut in the middle, the parts flew asunder with an explosion, the whole of the yellow portion disappeared, and gaseous chlorine was produced. When the end of the tube in which the yellow fluid lay was broken under water, there was also an immediate evolution of chlorine gas. The specific gravity of liquid chlorine is about 1.33. It is a non-conductor of electricity; its refractive power is rather less than that of water.—(*Phil. Trans.*, 1823, p. 160.)

Chlorine, when dry and pure is not affected by light, neither is it altered by exposure to very high temperatures. By means of the following apparatus, Sir H. Davy exposed it to the continued action of charcoal intensely ignited by voltaic electricity, without the smallest change in its properties. A glass globe (fig. 220), of about four inches diameter, has at its upper part a sliding wire passing air-tight through a ground collar, to the lower end of which is attached a piece of well-burned charcoal: at bottom is a stop-cock supporting a pincers, in which is another pointed piece of charcoal; the globe is exhausted upon the air-pump, filled with chlorine, and the stop-cock and sliding wire attached to the extremities of the voltaic apparatus; the charcoal points are then brought into contact by pushing down the upper wire, and they are thus retained as long as necessary in intense ignition.

Chlorine gas is of a greenish-yellow colour, a pungent and disagreeable smell, a peculiar and somewhat astringent taste, highly irritating and injurious when respired, and exciting cough and great irritation of the lungs, and mucous secretion from the trachea and bronchiæ, even when



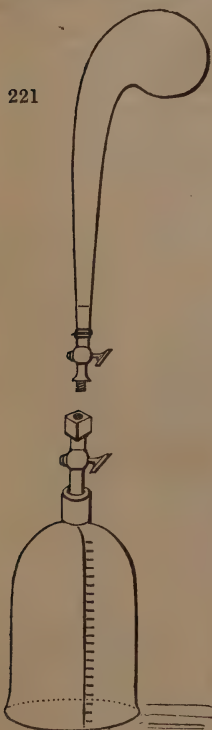
considerably diluted with atmospheric air. In some pulmonary complaints, the respiration of air slightly tainted by the admixture of chlorine has been resorted to as a stimulant. The specific gravity of chlorine compared with air, is, according to Gay Lussac and Thenard, 2·470, which gives 76·59 grains as the weight of 100 cubical inches at mean temperature and pressure. According to Thomson, the specific gravity of chlorine is 2·5, and at the temperature of 32° 100 cubic inches weigh 81·975 grains. According to Davy, 100 cubic inches weigh between 76 and 77 grains. Its specific gravity, in reference to hydrogen, may be considered as 36 to 1, (according to Berzelius 35·42, and according to Turner 35·84. *Elements of Chemistry*, fifth edit., p. 230.) Chlorine is an electrolytic anion.

At the temperature of 60°, water dissolves two volumes of chlorine. The solution has a specific gravity of 1·008; it is of a pale yellow colour, has an astringent, nauseous taste, and destroys vegetable colours: hence its use in bleaching: though the gas itself, when perfectly free from moisture, has scarcely any such action. Hence it is probable that the bleaching agency is due to the evolution of nascent oxygen resulting from the decomposition of water; and there are other compounds containing oxygen, but no chlorine, which are also bleaching agents, such as the peroxide of hydrogen, and manganic and chromic acids. The bleaching power of dew, and sometimes of rain-water, renders it probable that they also contain some excess of oxygen, perhaps in the form of the peroxide of hydrogen.

When aqueous solution of chlorine is exposed to the direct rays of the sun, oxygen is evolved in consequence of the decomposition of the water, the hydrogen of which unites to the chlorine, and forms hydrochloric acid. The same change ensues more slowly in common day-light, but in the dark there is no such decomposition. As gaseous chlorine generally contains aqueous vapour, the bottles in which it is preserved should be excluded from light.

Chlorine, and its aqueous solution, are powerful antiseptics, and destroyers of contagious and infectious matter, and of bad odours. This property depends upon the power which chlorine has of decomposing those noxious compounds, and resolving them into others which are harmless. For the purposes of fumigation, chlorine liberated from black oxide of manganese and hydrochloric acid, or from manganese, salt, and sulphuric acid, may be diffused through the atmosphere of the infected chambers; or the infected goods may be exposed to it. In the same way the offensive odours of dead bodies may be mitigated by sprinkling them with solution of chlorine. (Faraday, *Quar. Jour.*, xviii., p. 92. See Chloride of Soda, Chloride of Lime, &c.)

When a burning taper is immersed in a jar



of chlorine, the brilliancy of the flame is much impaired; it becomes red, throws off dense fumes and is soon extinguished. There are, however, many bodies, such as phosphorus and several of the metals, which are spontaneously ignited by chlorine, and burn in it with much brilliancy. In these cases, binary compounds result, some of which, like those of oxygen, are possessed of acid properties: others are not acid, and are termed *chlorides*. Brass or copper leaf, and powdered antimony, serve well to show the intense action of chlorine upon certain metals. When introduced into the gas, they enter into immediate combustion, and *chloride of copper* and *chloride of antimony* are formed. The most elegant way of making these experiments consists in introducing the phosphorus, or the copper leaf, into a retort (fig. 221), mounted with a stop-cock, and exhausted upon the air-pump; it is then screwed into the cap of an air-jar of chlorine, also mounted with a stop-cock, and standing over water. Upon opening the cocks, the gas rushes into the retort, and the phosphorus or copper leaf immediately burns. In consequence of their irregular thickness and form, retorts are frequently broken by the air's pressure whilst exhausting; so that it is safe to cover them with a cloth during the process, to prevent the splinters being thrown about. A piece of bibulous paper, dipped into oil of turpentine, is also spontaneously inflamed when put into a jar of chlorine.

The presence of chlorine is recognized by its bleaching power, by its odour and colour, and by its action upon solution of nitrate of silver, in which it occasions a white curdy precipitate, insoluble in nitric acid, but soluble in liquid ammonia, and speedily blackening by exposure to light. It is also detected by electrolytic action, as already shown (p. 308).

CHLORINE AND OXYGEN.—No compound of these two elementary substances can be obtained by their direct mutual action, for they have but a feeble affinity for each other, and, when combined, are easily separable. By presenting chlorine and oxygen, however, to each other, under certain conditions, they have been found to form four distinct compounds.

1. PROTOXIDE OF CHLORINE. HYPOCHLOROUS ACID. ($C + O$), or \dot{C} . In the *Phil. Trans.* for 1811, Sir H. Davy has described a peculiar gas, to which, on account of its deep yellow-green colour, he gave the name of *euchlorine*. He obtained it by mixing in a small retort, 2 parts of chlorate of potassa with 1 of water, and 1 of hydrochloric acid, and applying *a very gentle heat*, so as to cause a moderate effervescence: he collected it in small jars or tubes over mercury, but the best way of examining it is to retain it in the tube or vessel in which it is generated, or to collect it in a clean dry phial or jar, as described by fig. 222 at the foot of the next page.

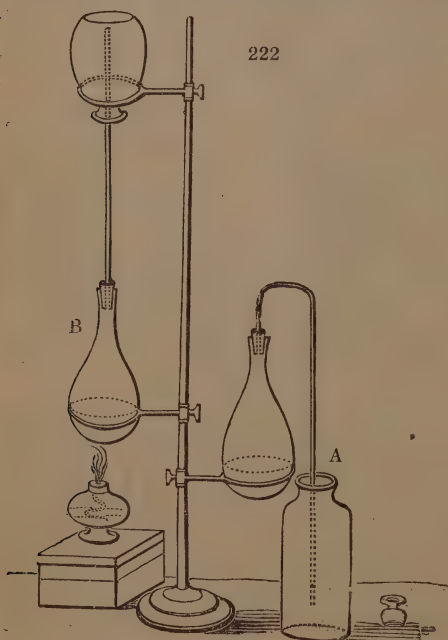
This gas has a peculiar odour, like diluted chlorine, and is pernicious to respiration. Davy found its specific gravity to vary; he estimated it at about 2.4: Gay Lussac and Thenard regard it as = 3. Water dissolves ten volumes of this gas, and acquires its peculiar odour, and a deep yellow colour; it destroys most vegetable colours, previously reddening some of the blues. Its most remarkable character is the facility with which it is decomposed: when gently heated in the upper part of a small tube standing over mercury, a kind of explosion, attended by a flash of light, ensues, and the tube is projected to some distance; but if it be firmly

held down in the mercury, the results of the decomposition are retained. According to Davy, 50 volumes are thus expanded to 60, consisting of a mixture of 40 of chlorine and 20 of oxygen. According to Gay Lussac, 1 volume becomes by decomposition $1\frac{1}{2}$, composed of 1 volume of chlorine and $\frac{1}{2}$ a volume of oxygen. According to this view, *protoxide of chlorine* would consist of

				Gay Lussac.	
				Volumes.	S. G.
Chlorine .	1 .	36 .	81.82	1.0 .	2.45
Oxygen .	1 .	8 .	18.18	0.5 .	0.55
	1	44	100.00	1	3.00

This gas sometimes explodes whilst it is collecting, or in being transferred from one vessel into another, or even by the heat of the hand, so that it should be cautiously dealt with and examined, and collected in small quantities only*. Detonated with hydrogen, in the proportion of five measures of the gas to eight of hydrogen, it gives rise to the production of water and hydrochloric acid. It is decomposed by all burning bodies, and their combustion continues as it would in a mixture of chlorine and oxygen in the above-mentioned proportions. A small piece of phosphorus let up into the gas instantly takes fire and absorbs it, burning with much brilliancy.

The experiments of Soubeiran (*Ann. de Chim. et Phys.*, xlviii., 113) rendered it probable that euchlorine is not a definite compound, but a mixture of chlorine with the peroxide of chlorine, an opinion which some of Sir H. Davy's observations appear to corroborate; at least he found that water resolved it into chlorine and peroxide of chlorine. Soubeiran



* There are certain gases which are absorbable by water, but which, being either heavier or lighter than atmospheric air, may with a little management be collected sufficiently pure by placing the materials for producing them in a flask, furnished with a tube of convenient length, and twice bent at right angles, so as to pass to the bottom of a clean stoppered phial: the disengaged gas, if heavier than the air, displaces it; when it is full, it must be cautiously withdrawn, and stopped, and another phial put into its place: see the wood-cut (fig. 222) A. If the gas thus to be collected is lighter than the atmosphere, the tube from the flask may be straight, and pass up into an inverted phial, as at B.

passed it over calomel, by which its excess of chlorine was absorbed and peroxide of chlorine was liberated. The nonaction of this gas on copper-leaf seems, however, to justify its being considered definite, although Davy found that a mere *mixture* of peroxide of chlorine with chlorine did not immediately act upon copper leaf.

Such was the extent of our information respecting the nature of this compound of chlorine and oxygen previous to the researches of Balard, who, in an elaborate paper on the nature of the bleaching combinations of chlorine (*Ann. de Chim. et Phys.*, lvii., 225; and Taylor's *Scientific Memoirs*, i., 269) has more fully investigated its properties, and shown the mode of obtaining it in a pure form; he has also proposed to designate it *hypochlorous acid*. His process consists in agitating a mixture of one part of finely-powdered red oxide of mercury with twelve of distilled water, in a bottle filled with chlorine; the gas is rapidly absorbed: if the proportion of the oxide is insufficient the deposited powder is white, and some of the chlorine remains unabsorbed; but the oxide should be in slight excess, so as to remain red, and entirely absorb the gas, (6 drachms of red oxide mixed in fine powder, with an ounce and a half of water, and shaken in a quart bottle of chlorine are the proportions recommended by Mr. Graham.) When the absorption is complete, the contents of the bottle are poured upon a filter, and the filtrated liquor subjected to distillation in vacuo, by which a diluted solution of hypochlorous acid is obtained, and which may be concentrated by a second distillation. After enumerating the properties of this liquid or aqueous acid, M. Balard proceeds to show the mode of obtaining from it the pure gaseous acid: this he effected by throwing up into an inverted jar of mercury a small quantity of the liquid acid, and then passing into it, through the mercury, small fragments of fused nitrate of lime; this salt abstracts the water and liberates the pure *hypochlorous acid* in the state of a gas, a little deeper coloured than chlorine, of a strong penetrating odour, and absorbable by mercury, from the contact of which it is preserved in the above mode of obtaining it, by the layer of solution of nitrate of lime. Water dissolves many times its volume, forming a pale-coloured solution, similar to that originally obtained by distillation in vacuo. A slight elevation of temperature is sufficient to decompose this gas, with explosion and evolution of heat and light, so that it requires careful management. It is not changed by some hours' exposure to diffused daylight, but direct solar rays decompose it in a few minutes without explosion: when mixed with hydrogen and inflamed, it detonates violently, but at common temperatures the mixture remains unchanged. Bromine and iodine slowly decompose it; sulphur, selenium, phosphorus, and arsenic decompose it with sudden and violent detonation; charcoal also causes it to explode, apparently in consequence of the condensation which the gas suffers in its pores. Blotting-paper introduced into the gas also causes its sudden decomposition into a mixture of chlorine and oxygen; indigo decomposes it slowly and with more complicated changes. By the action of oxalic acid it forms carbonic acid, and chlorine is evolved. M. Balard found, by various analytical methods, that the composition of this hypochlorous acid gas is analogous to that of Davy's *euchlorine*; that is, that it consists of 1 volume of chlorine and 0.5 volumes of oxygen, condensed into 1 volume; but he gives reasons which we shall again

advert to in speaking of some of the hypochlorites, for regarding the equivalent of the hypochlorous acid, not as $36 + 8 = 44$, but as $72 + 16 = 88$; that is, as consisting of

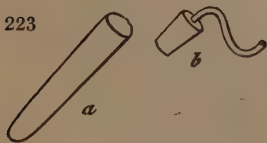
Chlorine	..	2	..	72	..	81.82
Oxygen	..	2	..	16	..	18.18
		—		—		—
		1		88		100.00

The aqueous solution of this acid is pale yellow; it has a peculiar penetrating odour, and an acrid but not acid taste; it attacks the cuticle with great energy, destroying it more rapidly than nitric acid, and communicating to it a reddish-brown-colour. It decomposes at common temperatures, and in summer requires to be kept in ice, and in a dark place. In the voltaic circuit it disengages oxygen, but no chlorine at the positive pole: the latter, no doubt, unites to the nascent hydrogen to form hydrochloric acid. It is rapidly decomposed by iron-filings, but of the other metals there are few which have any very energetic action upon it. It is curious that, with the exception of silver, they become oxidized and evolve chlorine; silver, on the contrary, evolves oxygen, and combines with the chlorine. It converts bromine and iodine into bromic and iodic acids; and sulphur, phosphorus, selenium, and arsenic, into their acids, with the evolution of chlorine. When a concentrated solution of this acid is mixed with ammonia, or when a fragment of sulphate or phosphate of ammonia is suspended in it, drops of the *explosive chloride of nitrogen* are formed: if both solutions are concentrated, effervescence and decomposition ensue.

PEROXIDE OF CHLORINE. CHLOROUS ACID. HYPOCHLORIC ACID. ($C + 4O$)

or $\overset{\cdot\cdot\cdot}{C}$, was discovered by Sir H. Davy, in 1815 (*Phil. Trans.*, p. 214). It is obtained as follows:—about 50 grains of chlorate of potassa are moistened with a few drops of concentrated sulphuric acid, and rubbed together with a platinum spatula, till they incorporate and form a solid mass of an orange colour. This mass is to be introduced into a small glass retort, and gradually warmed in a water-bath, the temperature of which must be carefully kept below 212° , which may be managed by mixing alcohol with the water. (Or we may use a small tube, sealed at one end, as a substitute for a retort, and fitted with a cork perforated by a small *S* tube,

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as in fig. 223, where *a* represents the tube, which should be wrapped round with a little tow, in case of explosion, to prevent fragments being thrown about; *b* the cork, &c.) A bright yellowish-green elastic fluid passes off, which is rapidly absorbed by water, but may be collected in small tubes

over mercury. The colour of this gas is more brilliant than that of the protoxide, and its odour peculiar, and unmixed with the smell of free chlorine. Its specific gravity, compared with air, is, according to Davy, as 2.360 to 1.000; theoretically 2.338; compared with hydrogen it is as 34 to 1, 100 cubic inches therefore should weigh, at mean temperature and pressure, 72.012 grains. When peroxide of chlorine is heated to a temperature somewhat below that of boiling water, it explodes with much violence and the evolution of a bright light. The result of

this decomposition is, that two volumes of the gas are expanded into three, two of which are oxygen, and one chlorine; the relative weights, therefore, of its elements, are 32 of oxygen and 36 of chlorine. It requires the same, and even greater precautions, in preparing and transferring, as the former gas*.

Its saturated aqueous solution (containing about 7 volumes of the gas to 1 of water) is of a deep yellow colour, an astringent and corroding taste, and when applied to the tongue, leaves for a long time a very disagreeable sensation. It destroys vegetable colours. It is absorbed according to Martens (*Ann. C. & P.*, lxi. 293,) by alkaline solutions, forming with them a peculiar class of bleaching salts.

Mr. Faraday condensed this gas by enclosing the mixture of chlorate of potassa and sulphuric acid in a sealed tube, and leaving them to act upon each other for twenty-four hours. In that time there had been much action; the mixture was of a dark reddish-brown, and the atmosphere within of a bright yellow colour. The mixture was then heated up to 100° , and the unoccupied end of the tube cooled to 0° : by degrees, the mixture lost its dark colour, and an ethereal-looking liquid condensed. It was not miscible with a small portion of the sulphuric acid which lay beneath it; but when returned on to the mass of salt and acid, it was gradually absorbed, rendering the mixture of a much deeper colour. "The peroxide of chlorine thus obtained is a very fluid transparent substance of a deep yellow colour. A tube containing a portion of it in the clean end was opened at the opposite extremity; there was a rush of euchlorine vapour, but the salt plugged up the aperture: whilst clearing this away, the whole tube burst with a violent explosion." (*Phil. Trans.*, 1823, p. 194.) Sir H. Davy found that, of the unmetallic combustible substances, phosphorus was the only one which spontaneously decomposed this gas: the phenomena were the same as with the protoxide of chlorine. Two volumes, detonated with five of hydrogen, produce water and hydrochloric acid. When absorbed by solution of potassa, chlorate of potassa and chloride of potassium are formed. According to Davy and Gay Lussac, this gas consists of

	Volumes.				S. G.	
Chlorine	1	..	36	..	52.9	..
Oxygen	4	..	32	..	47.1	..
Peroxide of chlorine	1		68		100.0	
					2	
						2.45
						2.22
						2.33

CHLORIC ACID ($C + 5O$) or C' , or \dot{C} .—In the compound which has been thus called by its discoverer, M. Gay Lussac (*Annales de Chimie*,

* For the purpose of illustration, in lectures, this gas may be conveniently obtained by putting a few grains of chlorate of potassa into the bottom of a tall narrow tube or jar (half an inch diameter and about twelve high), standing upon a foot, and carefully dropping in upon the salt, so as not to soil the sides of the tube, a little sulphuric acid: the peroxide of chlorine is immediately evolved (provided no explosion ensues), and its

weight causes it to expel the superincumbent air and fill the tube, from which, with a little management, it may be decanted into a tall glass containing copper-leaf, upon which it exerts no action; but a hot wire, dipped into the gas, causes it immediately to explode, and the metal then burns in the mixed oxygen and chlorine. A little jet of nitric oxide thrown in, produces the same effect, without explosion.

tom. xci., p. 108), the relative proportions of chlorine and oxygen are to each other as 36 to 40: chloric acid cannot exist independent of water or some base, and, therefore, its properties in the dry or anhydrous state are not known.

Chloric acid may be prepared by passing a current of chlorine through a mixture of oxide of silver and water. Chloride of silver is produced, which is insoluble, and may be separated by filtration. The excess of chlorine, which the filtered liquor contains, is separable by heat, and the chloric acid dissolved in water remains. Chloric acid may also be obtained by adding dilute sulphuric acid to a solution of *chlorate of baryta*, as long as it occasions a precipitate. The baryta is thus separated in the form of an insoluble sulphate, and the chloric acid remains in aqueous solution. Care must be taken to add no more sulphuric acid than is requisite; for any excess contaminates the chloric acid. If the exact proportion has been used, the chloric acid is neither rendered turbid by dilute sulphuric acid nor by chlorate of baryta. If either of these occasions a precipitate, they must be *carefully* added till the effect ceases; the clear liquid may then be decanted or filtered off. It may be concentrated by cautious evaporation.

Chloric acid is a sour liquid, and of a yellowish tint when highly concentrated. It forms no precipitate in any metallic solution. It reddens vegetable blues, but has no bleaching power. When added to a strong solution of potassa, crystals of chlorate of potassa are deposited. When concentrated, it acts powerfully, and even to ignition, upon paper, and some other dry organic bodies; it decomposes alcohol, with the formation of acetic acid. The most remarkable of its salts, which are now termed *Chlorates*, were formerly known under the name of *Oxymuriates*. When distilled at a high heat, it suffers a partial decomposition, and a portion of chlorine and oxygen are liberated. It is decomposed by hydrochloric and sulphurous acids, and by sulphuretted hydrogen; but those acids which are already saturated with oxygen do not act upon it. Its decomposition by hydrochloric acid is attended with the evolution of chlorine and the formation of water; by sulphurous acid, with the evolution of chlorine and the production of sulphuric acid; and by sulphuretted hydrogen, with the separation of chlorine and sulphur and the formation of water.—(See *Chlorate of Potassa*.) Chloric acid consists of

										Chenevix.	Gay Lussac.	Volumes.
Chlorine	..	1	..	36	..	47.4	..	45	..	46.8	..	1.0
Oxygen	..	5	..	40	..	52.6	..	55	..	53.2	..	2.5
<hr/>												
Chloric acid	.	1		76		100.0		100		100.0		

PERCHLORIC, OXYCHLORIC, OR HYPERCHLORIC ACID, ($C + 7O$) or C'' ,
 ...
 or \bar{C} , was discovered by Count Stadion (*Ann. de Chimie et Phys.*, viii.): it is procured by distilling *perchlorate of potassa* with its own weight of sulphuric acid, diluted with about a fourth part of water. At a temperature of about 280° , white vapours pass off, which condense in the form of a colourless liquid. It is a very stable compound, not decomposed by sulphuric or hydrochloric acid; nor by alcohol or organic bodies. When concentrated, its specific gravity is 1.6, and it boils at 392° . By distilla-

tion with strong sulphuric acid it may be obtained in the solid form and crystallized; in this state it hisses when thrown into water. (GAY LUSSAC. SERULLAS. MITSCHERLICH. *Ann. de Chim. et Phys.*, viii., ix., xlv., and xlix.) It consists of

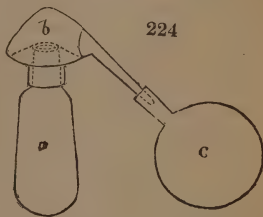
						Volumes.
Chlorine	...	1	...	36	...	39.1
Oxygen	...	7	...	56	...	60.9
Perchloric acid	1		92		100.0	

§ III. IODINE.

IODINE was discovered in 1812 by M. Courtois, a chemical manufacturer at Paris. Vauquelin (*Ann. de Chim.*, xc.), Gay Lussac (*Ibid.*, lxxxviii., xc., and xci.), and Davy (*Phil. Trans.*, 1814), have fully examined its properties.

Iodine is chiefly prepared at Glasgow from *kelp*, which is the fused ash obtained by burning sea-weeds, and is principally manufactured on the west coast of Ireland, and the western islands of Scotland. The long stems of the *Fucus palmatus* are most productive of iodine. "A high temperature in the preparation of kelp, which increases the proportion of alkaline carbonate, diminishes that of the iodine, owing to the volatility of the iodide of sodium at a full red heat. The kelp which contains most iodine, generally also contains most chloride of potassium, and it is for these two products that the substance is now valued, more than for its alkali."—(GRAHAM.)

Iodine may be procured by the following process: Lixivate powdered kelp with cold water. Evaporate the lixivium till a pellicle forms, and set aside to crystallize. Evaporate the mother-liquor to dryness, and pour upon the mass half its weight of sulphuric acid. Apply a gentle heat to this mixture in the flask *a* of the alembic shown in the annexed figure, of which *b* is the head or capital, having a tube issuing from it, and descending into the receiver *c*. Fumes of a violet colour arise, (hence its name, from *ιώδης*, *violaceus*,) and condense in the form of opaque crystals, having a metallic lustre; these are to be washed out of the head of the alembic with a small quantity of water, and quickly dried on bibulous paper.



Iodine may likewise be obtained from soap-makers' *black ash* by a similar process: instead of evaporating the mother-liquor to dryness, the quantity of iodine is sometimes greater when it is merely concentrated, mixed with excess of sulphuric acid, boiled, and filtered: the liquid is then mixed with its weight of powdered black oxide of manganese, and heated in an alembic, or in a flask with a wide tube attached to its neck, when the iodine sublimes as before.

According to Dr. Ure, iodine may be abundantly obtained from the brown residuary kelp-liquor of the soap-boilers, by exposing it to a heat of about 230°, saturating it with sulphuric acid previously diluted with

its bulk of water, and pouring the liquor, when cold, off the crystals which are deposited, and which are chiefly sulphate of soda. Filter this liquor, and to every 12 ounces by measure add 1000 grains of black oxide of manganese in powder; put this mixture into a large matrass with a wide neck, over which a glass globe is inverted, and apply heat with a charcoal chauffer. The less diffusive heat of a lamp is apt to crack the bottom of the matrass, particularly if a large quantity of materials be employed. To prevent the heat from acting on the globular receiver, a thin disc of wood, having a round hole in its centre, is placed over the shoulder of the matrass. As soon as the upper vessel becomes warm, another is to be put in its place, and thus the two may be used in rotation as long as violet fumes arise.

The process as conducted at Glasgow is described by Professor Graham in his *Elements of Chemistry*. Some useful directions respecting it are also given in the *Philosophical Magazine*, XL.

Traces of iodine are found in sea water, in sponge, in several saline springs, and in the coarser varieties of common salt; Vauquelin detected it in some silver ores from Mexico (*Ann. C. & P.*, xxix.); and Bustamente, in a white lead ore from Mexico, and in a species of *Agave*.—(*Ann. C. & P.*, Lxxii.)

Iodine has a bluish-black colour; its lustre is metallic, and its fracture when in a mass is greasy and lamellar. It is a non-conductor of electricity. It is not changed by passing through a red-hot tube, either alone or over charcoal. It is soft and friable. Its specific gravity according to Thomson is 3.08; according to Gay Lussac, 4.946. Its specific heat = 0.05412. (REGNAULT.) It produces a yellow stain upon the skin. Its smell somewhat resembles that of diluted chlorine; its taste is acrid. It is extremely volatile when moist, and in that state produces a pale violet vapour at a temperature between 60° and 80°. At 120° or 130° it rises more rapidly in vapour; at 220° it fuses; and at 350° it boils and produces dense violet-coloured fumes, which condense in brilliant plates, and acute octoëdrons. 100 cubical inches of iodine vapour weigh 270 grains. Its specific gravity, therefore, compared with air, is 8.7, and with hydrogen, 126. The density of iodine vapour, deduced from that of hydriodic acid is 8.7882. (THOMSON.) Like chlorine and oxygen, it is evolved from its combinations at the positive electrode; it renders vegetable colours yellow, and is very sparingly soluble in water, that liquid not holding more than one 7000th its weight in solution. The colour of this solution is pale brown; it gives out no oxygen by exposure to sunshine, nor does it bleach; it however slowly loses its own colour, and gives rise to the formation of *iodic* and of *hydriodic acid*. Iodine is much more soluble in alcohol and in ether, forming deep brown solutions.

The peculiar appearance of the vapour of iodine is in many cases a sufficient evidence of its presence; a more delicate test, however, was discovered by Messrs. Colin and Gaultier de Claubry, in its remarkable property of forming a deep blue insoluble compound with starch. According to Professor Stromeyer, a liquid, containing one 450,000th its weight of iodine, receives a blue tinge when a solution of starch is added to it. To ensure success, the iodine must be in a free state, and the

solution cold, for boiling water destroys the colour; where the proportion of iodine is very minute, a few minutes elapse before the discoloration ensues. (STROMEYER, in GILBERT's *Annalen*, xix. 146.) As the iodic compounds are decomposed by chlorine, it may often be conveniently used as a test of iodine. Thus, when a very minute quantity of iodide of sodium or potassium is present in a solution, the addition of chlorine discolours it, and if a little solution of starch be then added, the iodine is immediately detected by the blue colour. Or any compound containing common salt, and an alkaline iodide, mixed with a solution of starch, and exposed to voltaic action, yields a blue colour at the positive electrode. The equivalent of iodine may be assumed as = 126 (126.3, TURNER; 126.57, GRAHAM).

The principal use as yet made of iodine and its compounds, is in medicine; it powerfully promotes the action of the absorbents, and is chiefly used in glandular diseases, and as an alternative. In overdoses it is an irritant poison. The rich colour of some of its metallic combinations has led to its employment in the art of calico-printing.

Iodine is occasionally adulterated by plumbago, sulphuret of antimony, or peroxide of manganese, but these additions are easily detected by their insolubility in alcohol. The relative quantity of moisture in iodine may be ascertained by heating it in a tube, with twice its weight of fused chloride of calcium, at a temperature not exceeding the boiling-point of the iodine; the iodine may be expelled by a current of air and the increase of weight sustained by the chloride gives the quantity of water.

IODINE AND OXYGEN.—There appear to be four definite compounds of iodine with oxygen; an oxide, and three acids.

OXIDE OF IODINE.—This compound was discovered by Professor Sementini, in attempting the direct combination of iodine and oxygen: a portion of it, he says, is formed when iodine is repeatedly heated in atmospheric air, but it is most rapidly produced by presenting iodine and oxygen to each other at a high temperature. For this purpose, a bladder of oxygen is affixed to one end of a copper tube, so placed as to be heated red-hot by lamps or a small charcoal fire; the other end of the tube terminates in the bulb of a tubulated retort containing iodine, which is also to be heated by a lamp: the oxygen is then propelled through the hot tube into the vapour and upon the hot iodine, and a yellow and very thick oleaginous liquid distils over, of an acrid, disgusting taste and odour, which is the compound in question. It slowly volatilizes in the air, and is very soluble in water and alcohol, producing amber-coloured solutions. Phosphorus and potassium are inflamed by it. It changes the blue of litmus to green. If an alkali be poured into its solution, it is rendered colourless.

IODOUS ACID.—If excess of oxygen, and a considerable degree of heat, be employed in the preceding experiment, the product is partly *iodous acid*. This acid is best obtained by introducing a mixture of one part of iodine and three of chlorate of potassa into a retort, and rapidly applying heat: a dense fluid distils over, which should be collected in a receiver cooled by a freezing-mixture. It has a pungent taste and peculiarly disagreeable odour: its specific gravity exceeds that of water. It reddens litmus, and forms a yellow solution when diluted with water; it slowly

evaporates when exposed to air, and rapidly volatilizes at 112° . It is decomposed by sulphur, disengaging a little heat, and liberating violet vapours; sulphurous acid also decomposes it. Phosphorus and potassium are instantly inflamed by it. It is without action on carbon. It dissolves iodine. Neither its composition, nor that of the oxide, have been accurately determined. (*Quarterly Journal*, xvii. 381: *Ibid. New Series*, i. 477.) It appears probable, from the experiments of Wöhler, that the compound obtained when chlorate of potassa is used, contains chlorine. By the spontaneous evaporation of a solution of iodine in a dilute solution of soda, Mitscherlich obtained prismatic crystals, which by the action of hot water were converted into iodate of soda and iodide of sodium: he considers them as an *iodite* of soda.—(*Ann. de Chim. et Phys.*, xxxvii. 84.)

IODIC ACID ($i + 5o$) or i' , or $\overset{\cdot\cdot\cdot}{\text{I}}$ (DAVY, *Phil. Trans.*, 1815.)—This compound cannot be obtained by the direct action of oxygen on iodine, but it is formed by acting upon peroxide of chlorine by iodine. For this purpose the iodine may be introduced into a small flask, and the peroxide of chlorine disengaged upon it, from a proper mixture of chlorate of potassa and sulphuric acid, with the precautions above pointed out: or 100 grains of chlorate of potassa may be introduced into a small retort, with 400 grains of hydrochloric acid, of the specific gravity 1.105: annex to the retort a small globular receiver, having a bent tube issuing from it, and passing to the bottom of a small flask, containing about 50 grains of iodine; carefully apply the heat of a lamp to the retort, by which oxide of chlorine will be disengaged, and which will be decomposed and absorbed by the iodine. A compound is thus formed, which consists of chloride of iodine and iodic acid. The former is separable by a gentle heat; the latter remains as a white, deliquescent, semitransparent, sour, and inodorous body, very soluble in water, and of a specific gravity exceeding 2. Iodic acid may also be precipitated by slowly adding excess of sulphuric acid, or of alcohol, to the aqueous solution of the perchloride of iodine. This acid is also formed according to Mr. Connell, by boiling iodine for several hours with about five times its weight of strong nitric acid. The mixture should be introduced into a tube closed at one end, and the iodine, as it sublimes to the upper part, constantly returned into the acid, till it disappears: on carefully driving off the nitric acid by heat, the iodic acid remains. Iodic acid is also obtained by the decomposition of *iodate of soda* by sulphuric acid, (SERULLAS, *Ann. de Ch. et Ph.*, xliii. 216,) or *iodate of baryta* may be similarly treated.

The aqueous solution of iodic acid first reddens and then destroys vegetable colours; concentrated by evaporation, it affords a pasty mass, which is *hydrated iodic acid*, which may be crystallised in hexagonal laminæ, and from which the water may be driven off by the careful application of a higher temperature; at about 500° it fuses, and is decomposed into oxygen and iodine. It acts powerfully upon the metals, and with the oxides forms a class of salts called *iodates*. Nitric, sulphuric, phosphoric, and boracic acids, when dropped into a hot saturated solution of iodic acid, form crystals of a yellowish colour, composed of the two acids. (On the Salts of the Iodic Acid, see C. RAMMELSBERG, in *Poggend.* xliv. 525.) It is decomposed by hydrochloric and oxalic acids.

When iodic acid is mixed with charcoal, sulphur, and some other combustibles, it forms compounds which deflagrate when heated: its compounds also deflagrate, like the chlorates, when thrown upon red-hot charcoal. Iodic acid is composed, according to Gay Lussac, of

Iodine	. .	1	. .	126	. .	75.9
Oxygen	. .	5	. .	40	. .	24.1
<hr/>		<hr/>		<hr/>		<hr/>
Iodic acid	. .	1		166		100.0

OXIODIC ACID. PERIODIC ACID. ($i + 7O$), or i'' , or I . When a solution of iodate of soda, mixed with pure soda, is saturated by chlorine, and concentrated by evaporation, a sparingly soluble white salt is obtained, which is a *periodate of soda*: when it is dissolved in dilute nitric acid, and mixed with nitrate of silver, a yellow precipitate falls, which, dissolved in hot nitric acid and evaporated, yields orange-coloured crystals of *periodate of silver*. These crystals are decomposed by cold water, a yellow insoluble *subperiodate* of silver falls, and an aqueous solution of pure periodic acid is formed, which yields crystals of the *hydrated periodic acid* by evaporation, and which, at a temperature above 212° , are resolved into oxygen and iodic acid. (AMMERMÜLLER and MAGNUS: POGGENDORF'S *Annalen*, xxviii. 514.) The periodic acid consists of

Iodine	. .	1	. .	126	. .	69
Oxygen	. .	7	. .	56	. .	31
<hr/>		<hr/>		<hr/>		<hr/>
Periodic acid	. .	1	. .	182	. .	100

IODINE AND CHLORINE. CHLORIDE OF IODINE. CHLORIODIC ACID.—When chlorine is conducted into a vessel containing iodine, it is quickly absorbed, and a compound obtained, which is brown when the iodine is in excess, colourless when exactly saturated, and yellow if there be excess of chlorine. It is volatile, and may be distilled without decomposition. It tastes sour, and powerfully reddens litmus: it attracts moisture from the air, and dissolves readily in water, forming a brown solution when there is excess of iodine. It appears to decompose water, and to form hydrochloric acid and a compound of iodine and oxygen; but these combinations are not permanent, for, on evaporation, chlorine is evolved, and iodine liberated. The saturated compound is regarded as containing one volume of iodine, and two of chlorine. (BERZELIUS, i. 258.) Sir H. Davy (*Phil. Trans.* 1814, p. 487) described the crystalline compound obtained by subliming excess of iodine in chlorine, under the name of *chlorionic acid*, and regarded it as a compound of one proportional of iodine and one of chlorine. It forms no permanent compounds with salifiable bases.

The experiments of Dumas and Serullas seem to prove the existence of two compounds of chlorine and iodine, formed by passing chlorine over iodine. The *protochloride* is soluble without decomposition, in water, alcohol, and ether; but the *perchloride* is resolved by water into hydrochloric and iodic acids, the latter of which may be thrown down by sulphuric acid, or by alcohol. The exact composition of these chlorides has not yet been ascertained. (SOUBEIRAN, *Journ. de Pharm.*, Feb. 1837; KANE, *Phil. Mag.*, x. 430.)

§ IV. BROMINE.

THIS singular substance, first described in the *Annales de Chim. et Physique*, for August, 1826, was discovered by M. Balard of Montpellier. Bromine was originally obtained from the uncrystallizable residue of sea-water commonly called *bittern*; a current of chlorine passed through this liquid immediately gives it an orange tint, in consequence of the evolution of bromine from its combinations: a portion of sulphuric ether is then shaken up with it, which, as it separates upon the surface, is found to have abstracted the bromine, and acquired a reddish-brown tint. The ethereal solution is agitated with solution of potassa, by which bromate of potassa and bromide of potassium are formed, and the whole being evaporated to dryness, and exposed to a dull-red heat, leaves *bromide of potassium*. The solution of this salt is decomposed by passing chlorine into it, or by mixing it with a strong solution of chlorine; chloride of potassium is formed, and the bromine, being volatile, may be separated by distillation, and condensed in a receiver cooled by ice.

Bromine probably exists in sea-water in the state of bromide of magnesium, but its relative proportion is exceedingly minute. One hundred pounds of sea-water taken up at Trieste, afforded, by M. Balard's process, 5 grains of bromide of sodium = 3·3 grains of bromine. It would appear, that in the sea-water at Trieste the bromine is unaccompanied by any iodine; and the same is the case, according to M. Hermbstadt, with the waters of the Dead Sea. In the water of the Mediterranean, on the contrary, iodine is always found with bromine. Bromine is most readily recognised by evaporating the water, so as to separate all its more ordinary crystallizable contents, reducing the remainder to a very small bulk, and dropping in a concentrated solution of chlorine. In the absence of iodine, which may be detected by starch, the appearance of a yellow tint announces bromine. It has thus been discovered, not only in the waters of the ocean, but in certain salt springs, in the ashes of marine plants, and in those of some marine animals. Among the saline springs most abundant in bromine are those of Theodorshall, near Kreutznach in Germany; these are now the chief source of bromine as an article of commerce.

At common temperatures and pressures bromine is a deep reddish-brown liquid, of a peculiarly suffocating and disagreeable odour, whence its name (from *βρωμος*, *graveolentia*). Its specific gravity is about 3. It emits a brownish-red vapour at common temperatures, and boils at 116°. At a temperature somewhat below 0° it congeals into a brittle solid. It is a non-conductor of electricity, and appears in the Voltaic circuit at the positive electrode. It suffers no change by transmission through red-hot tubes. It dissolves sparingly in water, and forms under certain circumstances a definite *hydrate*, which according to Löwig (POGGENDORF's *Annalen*, xiv. 114) is obtained by exposing bromine with a small quantity of water to a temperature of 32°; red octoëdral crystals of the *hydrate of bromine* are then deposited, which continue permanent at the temperature of 50°. At a higher temperature they decompose into liquid bromine and aqueous solution of it. The hydrate is also obtained by passing the vapour of bromine through a moistened tube cooled nearly to the freezing-point. Bromine dissolves in alcohol, and more abundantly in ether. It destroys

vegetable colours. When a burning taper is immersed into its vapour it is speedily extinguished, the flame previously assuming a green and red tint. Phosphorus spontaneously inflames in its vapour; tin and antimony also burn in it; and it combines with potassium with explosive violence. Its action on alkaline solutions will be found analogous to that of chlorine and iodine. It stains the skin of a yellow colour; acts with energy upon most vegetable and animal substances; and is fatal to animal life; a single drop placed upon the beak of a bird immediately killed it. The specific gravity of its vapour has not been correctly determined, but its equivalent number appears, from Berzelius' analysis of bromide of silver, to be about 78, which ought also to express its specific gravity in vapour compared with hydrogen. The density of its vapour compared to air, will, therefore, be about 5·4, and 100 cubical inches should weigh about 167 grains. According to Dr. Thomson the density of bromine vapour theoretically deduced is 5·555. The alcoholic solution of bromine, and the bromide of sodium are occasionally used in medicine: and from its powerful action, there can be no doubt that it must contribute to the medicinal virtues of the mineral waters in which it exists.

BROMINE AND OXYGEN—BROMIC ACID. ($b + 5 o$) or b' , or Br. One compound only of bromine and oxygen has as yet been discovered, namely, the *bromic acid*. Bromic acid is obtained by the decomposition of a solution of *bromate of baryta* by sulphuric acid: sulphate of baryta is precipitated, and a solution of bromic acid obtained, which may be concentrated by slow evaporation; at a high temperature it is partly decomposed, and it cannot be obtained anhydrous. It is sour, inodorous, and first reddens, and then destroys the blue of litmus. It is partially decomposed by concentrated sulphuric acid, but not by nitric acid. It is decomposed by sulphurous acid, by sulphuretted hydrogen, and by hydriodic and hydrochloric acids. From the analysis of bromate of potassa there can be no doubt that the bromic acid is analogous in composition to the chloric and iodic acids, and that it consists of

Bromine	...	1	..	78	..	66·1
Oxygen	..	5	..	40	..	33·9
<hr/>						
Bromic acid	..	1	..	118	..	100·0

CHLORIDE OF BROMINE.—By passing chlorine through bromine, and condensing the vapours at a low temperature, a reddish-yellow fluid is obtained, having a penetrating odour and disagreeable taste. It is very fluid and volatile, emitting yellow vapours; it dissolves in water, and the solution destroys vegetable colours: it would appear, therefore, not to decompose water. Chlorine decomposes most of the compounds of bromine, and hence is useful as a test of its presence. When, for instance, aqueous chlorine is dropped into a weak solution of bromide of potassium, or of sodium, the evolution of bromine is manifested by the deep yellow colour that is produced, and by the odour of the vapour of bromine.

IODIDE OF BROMINE.—Iodine and bromine probably combine in two proportions, but the compounds have not been analyzed. In certain proportions (probably one proportional of iodine and one of bromine) a solid body is obtained, which yields reddish-brown vapours when heated, and these readily condense into arborescent crystals. A further addition of

bromine dissolves these, forming a dark-coloured liquid, soluble in water, possessed of bleaching qualities, and yielding bromides and iodides with the alkalis.

Chlorine, iodine, and bromine, are occasionally so associated as to require separation in analyses. To ascertain the quantity of iodine in the mixed chlorides and iodides of mineral waters, Rose recommends precipitation by nitrate of silver; the mixed chloride and iodide of silver thus thrown down is fused, weighed, and afterwards heated in a tube and a stream of chlorine passed over it; the iodine is thus expelled, and the whole converted into chloride of silver; this is weighed again, and a loss is found to have taken place in consequence of the equivalent of the expelled iodine being greater than that of the expelling chlorine; this loss, multiplied by 1.389, gives the quantity of iodine originally present, and which has been replaced by the chlorine. Schweitzer recommends the adoption of a similar method for estimating the quantity of iodine when mixed with bromine; in this case the mixed iodide and bromide of silver is to be heated in an atmosphere of bromine vapour, by which the iodine is expelled. But the accurate determination of the relative quantities of chlorine, bromine, and iodine, in cases where their combinations are blended, is a problem of much difficulty.

§ V. FLUORINE.

THIS substance has not hitherto been obtained in an insulated state, for its powers of combination are such, that no body has been found capable of resisting its energetic action. The evidence of its existence, as a distinct electro-negative element, will be more clearly understood by reference to the account of its compound with hydrogen (See HYDRO-FLUORIC ACID), and to the experiments of Sir H. Davy (*Phil. Trans.*, 1813, p. 263, and 1814). Its equivalent number is probably = 16. It is found as a component part of a few mineral substances only; one of these, however, commonly called *fluor-spar*, is very abundant and appears to be a compound of fluorine and calcium, or a *fluoride of calcium*. Traces of fluorine are supposed to have been found in bone and in the enamel of teeth. No compound of fluorine with oxygen, chlorine, iodine, or bromine, has yet been satisfactorily shown to exist*.

It may be remarked of the bodies which have been above described that although they do combine with each other, they are not possessed of powerful mutual affinities; and, consequently, their compounds are, with few exceptions, either unstable, or easily decomposed; this is what might be expected as a consequence of their analogous electrical relations; for they are all apparently evolved at the anode in Voltaic arrangements. Yet, in respect to each other, it has been supposed that they may exhibit opposite, though feeble electrical energies, and that such compounds, in Voltaic decomposition, may thus present one of their elements at the negative electrode; a mixed solution, for instance, of bromine and iodine, when electrically decomposed, is stated to evolve

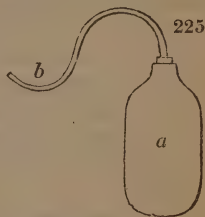
* Baudrimont, and the Messrs. Knox, have each published experiments by which they state that fluorine may be isolated. (*Phil. Mag.* 3rd series, vol. ix. x. and xii.) "But more than one skilful chemist of name has been less fortunate in obtaining indications so decisive, of the isolation of fluorine." (GRAHAM.)

bromine at the positive, and iodine at the negative surface, and it has hence been concluded, that iodine is electro-positive in respect to bromine; but the possible influence of secondary electro-chemical action, in these cases, has not been taken into the account. The compounds of the bodies above described with hydrogen and with the metals, when subjected to electrical decomposition, give up the inflammable body at the negative pole, or cathode, while the supporter of combustion appears at the positive pole, or anode.

§ VI. HYDROGEN.

HYDROGEN was first duly examined in a pure state by Mr. Cavendish, in 1766. (*Phil. Trans.*, vol. lvi. 144.) It had before been confounded with several of its compounds, under the name of *inflammable air*: the term *hydrogen* was given to it by the French chemists in consequence of its being one of the elements of water (from *ὕδωρ*, *water*, and *γεννέω*, *to generate*). It also forms a component of all vegetable and animal products, and is therefore abundantly diffused throughout nature.

Hydrogen gas may be obtained by the action of iron or zinc upon dilute sulphuric acid. Some pieces of iron-wire, or of zinc, may be introduced into the tubulated flask *a* (fig. 225), and covered with sulphuric acid diluted with six times its bulk of water; an effervescence ensues, heat is evolved, and the gas escapes by the bent tube *b*, inserted by grinding into the neck of the flask, and may be collected in the hydro-pneumatic apparatus. The hydrogen, however, which is thus obtained, is never perfectly pure. When procured by the means of iron, its odour is peculiarly disagreeable, in consequence, according to Berzelius (*Lehrbuch*, 186), of its containing a portion of volatile oil, formed by its union with a minute quantity of carbon which all common iron contains. When such gas is passed through alcohol, much of the odour is absorbed by it, and on diluting it with water, it becomes milky. Obtained by means of zinc, the gas is perhaps somewhat more pure, but it appears to hold a trace of zinc in solution, and often traces of sulphur and of arsenic. For the purposes of delicate experiments, hydrogen must be passed through a solution of potassa, then dried by passing it through a tube containing fragments of fused chloride of calcium; it should also be collected over mercury, and procured from purified zinc, and sulphuric acid so far diluted as to act but slowly upon the metal. The hydrogen liberated by the Voltaic decomposition of water by platinum surfaces (see WATER), may, when dried, be considered as absolutely pure. Upon the same principle it may be obtained by inverting a platinum crucible in dilute sulphuric acid, and placing a plate of zinc upon it; the hydrogen is then evolved by the Voltaic action of the two metals, and a portion of it collects within the crucible. This gas is also in a state of extreme purity when liberated from pure water by the action of an amalgam of potassium or of sodium.



Hydrogen is an uncondensable æriform fluid, not absorbable by water, unless that liquid has been previously deprived, by boiling, of common air, in which case 100 cubic inches dissolve about 1.5 cubic inches of

the gas. It has no taste, and when perfectly pure, is inodorous, but it usually has a slight disagreeable smell. It has great power of refracting light (p. 193.) It may be respired for a short time, though it is instantly fatal to small animals. M. Maunoir, after having breathed a quantity of pure hydrogen, found that his voice had become remarkably shrill. (*Phil. Mag.*, iv. 214.) The intensity of sound is greatly diminished in an atmosphere of hydrogen; Leslie, indeed, found it more feeble than its rarity compared with air would have led him to expect. He placed a piece of clock-work by which a bell was struck every half minute under the receiver of the air-pump, and, after exhausting the air, filled the receiver with hydrogen, but the sound was then even feebler than in the highly-rarified atmosphere. (*Ann. Philos.*, 2nd series, iv. 172.) It is stated that sound moves at least three times as fast in hydrogen as in air.

Hydrogen gas is the lightest known form of matter, and its equivalent or atomic weight is below that of all other substances, it is, therefore, conveniently assumed as *unity* in speaking of the specific gravity of gases, as well as in referring to the proportions in which bodies combine. In consequence of its extreme lightness, it is difficult to determine its weight with accuracy by the common process; but the researches of Berzelius and Dulong, and of Dr. Prout, lead us to infer that its specific gravity, compared with oxygen, is as 1 to 16: 100 cubic inches, therefore, of pure hydrogen gas at mean temperature and pressure weigh only 2.1318 grains, and compared with air, its specific gravity is as 0.0694 to 1. At the temperature of 32° 100 cubic inches weigh 2.22756 grains. (THOMSON.)

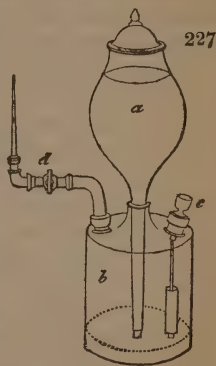
The low specific gravity of hydrogen is well and amusingly illustrated by substituting it for common air, in soap bubbles, which then rapidly ascend in the atmosphere, and may be kindled by the flame of a taper. The same circumstance also led to its employment for the inflation of balloons, which, however, have of late years been generally filled with coal-gas. Small balloons may be purchased, made of gold-beater's skin, or of the lining membrane of the crop of a turkey, which, when filled with pure hydrogen, rise to the ceiling, their specific gravity being inferior to that of the surrounding air. Some of these when filled with hydrogen, do not weigh more than 42 grains, while the same bulk of air would weigh 52 grains, so that their buoyant power is about = 10 grains.



Hydrogen is inflammable, and extinguishes flame. When pure, it burns quietly, with a lambent blue flame at the surface in contact with air; but, if mixed with thrice its volume of air, it burns rapidly, and with detonation. In making this experiment, a strong phial, capable of holding about six ounces of water, may be employed; or the *inflammable air-pistol*, which admits of the mixture being fired by the electric spark. This instrument consists of a cylinder of brass, about three-fourths of an inch diameter, and six inches long, in the form of a small cannon or pistol-barrel, properly mounted and having a wire, *a* (fig. 226), at the part usually occupied by the touch-hole, passing through a

tube of ivory, *b*, and not quite touching the interior of the cylinder; an electric spark communicated to this wire inflames the mixture of hydrogen and atmospheric air in the interior. It may be charged, by previously filling it with dry sand, and emptying it out into a phial of hydrogen, which then rises into the gun sufficiently mixed with air; the muzzle may be secured by a cork, which is expelled with much violence and a loud report, upon the inflammation of the gas.

The electrical air-gun may be also charged, by holding it for a moment over the open jet of the following instrument, (fig. 227,) always taking care that there is a due admixture of atmospheric air, otherwise the electric spark will not inflame it. *a* is a funnel-shaped vessel, fitting by a ground-joint into the three-necked bottle *b*; to the stopper *c* is annexed a brass wire, with a cylinder of zinc screwed upon its lower end; *d* is a tube furnished with a stopcock and jet-pipe; the capacity of the vessel *a* should be nearly equivalent to that of *b*, and may contain from one to three or four pints. To charge this apparatus with hydrogen, *b* is three-fourths filled with water, and the stopper *c* being removed, a quantity of sulphuric acid, previously diluted with its bulk of water, is poured in by a long funnel, so that it may remain at the bottom of the water which now fills the vessel. The stopper *c*, with its appended piece of zinc, is then put in, and the generated hydrogen forces the dilute acid into *a*, where its pressure serves to propel the gas through *d*, whenever the stop-cock is opened; the acid, at the same time descending, produces a fresh portion of hydrogen by again acting upon the zinc. This instrument is useful where small quantities of hydrogen are required for burning, charging air-guns, and other purposes.



Volta's air-lamp, in which a jet of hydrogen is inflamed by a small spark, furnished by an electrophorus concealed in the foot of the apparatus, also furnishes an elegant illustration of the ready inflammability of hydrogen by the electric spark.

In examining into the quantity of atmospheric air required to form an explosive mixture with hydrogen, Mr. Cavendish found the loudest report was produced by two volumes of hydrogen with six of air. One of hydrogen with nine of air burned very feebly, and four of hydrogen with one of air burned without explosion. (*Phil. Trans.*, Lvi.)

The inflammability, as well as the low specific gravity of hydrogen, are shown in the following experiments:—Let a jar filled with this gas stand for a few seconds, with its open mouth upwards; on letting down a candle, the gas will be found to have escaped, and to be replaced by common air. Place another jar of the gas inverted, or with its mouth downwards; the gas will now be found to remain a short time in the jar, being prevented from escaping upwards by the bottom and sides of the vessel. (HENRY.) Provide an air-jar, with a stopcock and jet, and fill it with hydrogen, upon the shelf of the pneumatic trough; then set fire to the gas at the jet, and whilst it is there burning, slowly lift the jar out of the water, and hold it firmly by the brass cap. The flame will continue for

some time at the jet, the hydrogen being propelled through it by its lightness; but when the air becomes mixed in such proportions with the gas as to form an explosive mixture, the flame recedes through the jet, and the whole kindles suddenly. (BERZELIUS.) Hydrogen may in fact be decanted, as it were, *per ascensum*, from one jar into another held above it. Thus, if a light bell-glass be suspended with its mouth downwards to one end of a scale-beam, and accurately counterpoised, it will be found, on placing a jar of hydrogen gas closed by a plate of glass underneath it, that the hydrogen, on removing the glass plate, will ascend into the bell, and, by its lightness, cause the counterpoise to sink; the hydrogen may also be inflamed by a taper introduced into the counterpoised bell.

If, instead of a mixture of hydrogen and atmospheric air, two volumes of hydrogen mixed with one of *oxygen* be burned in the air-gun, or in a stout and small phial, the explosion is extremely violent; but if the mixture be diluted with eight measures of hydrogen, or with nine of oxygen, it becomes unflammable.

If a current of hydrogen be inflamed when issuing from a small aperture, and a tube of eighteen or twenty inches in length be held over the flame, as in fig. 228, a peculiar musical tone is produced, varying in its pitch with the length and diameter of the tube, and the extent to which the flame, which should be very small, is introduced within it. This effect is not peculiar to hydrogen, but is produced by a variety of other flames (FARADAY, *Journal of Science and the Arts*, vol. v.), and is referable to the succession of explosions and consequent vibrations produced by the combustion of the gas in the tube.



The tendency which gaseous fluids have to become completely mixed under all circumstances, and as it were to penetrate each other, is well illustrated where hydrogen is employed. Thus, if two small phials, the one containing oxygen and the other hydrogen, be connected perpendicularly by a long glass tube, of small bore, it will be found, that although the hydrogen be uppermost, and much lighter than the oxygen, it will, in the course of a few hours, have perfectly mixed with the oxygen, and the gases will be found in equal proportions in both phials: hence the expression that one gas acts as a vacuum with respect to another. (DALTON, *Manchester Memoirs*, vol. i., New Series.)

The facility, too, with which hydrogen passes through crevices, fissures, and capillary tubes, as also through membranes and various organic tissues, is very remarkable. Attention was first called to this subject by a curious observation of Döbereiner on the escape of hydrogen through a small crack or fissure in a glass jar, which had been filled with the gas, and placed upon the shelf of the pneumatic trough; to his surprise, the water rose in the jar nearly three inches above the level of that in the trough. The subject was afterwards investigated by Professor Graham, who published a masterly essay upon it in the *Edinburgh Philos. Trans.* (xii. 222.) The following is an abstract of his inquiries, abridged from his *Elements of*

Chemistry. On examining Döbereiner's result, he found that while the hydrogen escaped outwards, a portion of air penetrated inwards, amounting to between one-fourth and one-fifth of the volume of the lost hydrogen: that, in fact, when hydrogen communicates with air by such a chink, there is a powerful disposition to mutual intermixture; "a particle of air, however, does not interchange with a particle of hydrogen of the same magnitude, but of 3.83 times its magnitude. We may adopt the word *diffusion-volume* to express this diversity of disposition in gases to interchange particles, and say that the diffusion-volume of air being = 1, that of hydrogen gas is = 3.83. Now every gas has a diffusion-volume peculiar to itself, and depending upon its specific gravity: of those gases which are lighter than air, the diffusion-volume is greater than 1, and of those which are heavier, the diffusion-volume is less than 1."

Professor Graham's results were obtained by what he calls a *diffusion-tube*; it is a graduated glass tube of about half an inch diameter, and fourteen inches long; one end is closed by a plate of plaster of Paris of about one-fifth of an inch thick; it may be used over mercury or water, but in the latter case care must be taken in filling it, to keep the plaster plug dry. When this tube is filled with hydrogen gas, standing over water, the gas diffuses into the atmosphere through the pores of the stucco, the water rises proportionately in the tube, and in about half an hour, the whole of the hydrogen will have escaped, and a certain quantity of common air entered: in experiments for determining the proportion of gas diffused and of replacing air, inequality of pressure must be guarded against by placing the diffusion-tube in a jar of water which must be filled up in proportion as it rises in the tube, and the inner and outer levels kept equal. Assuming the diffusive power of air as = 1, that of hydrogen is = 3.8; of oxygen = 0.9; of nitrogen = 1.014.

Cork, spongy platinum, and other porous substances, may be substituted for the stucco, in the diffusion-tube; or a piece of bladder, or thin caoutchouc, may be used. With the latter a very striking experiment, illustrative of this form of *endosmose* and *exosmose*, may be made as follows:—confine a portion of common air in a tumbler or wide-mouthed jar, by tying it carefully over with a piece of thin sheet-caoutchouc, and place it under a large bell-glass filled with hydrogen gas, and standing in a dish of water: the hydrogen will gradually find its way through the caoutchouc and act upon it with such elastic power as forcibly to distend and even ultimately burst it. If the small jar be filled with hydrogen, and the larger one with air, an opposite result will ensue, as shown by the concave instead of convex surface assumed by the elastic diaphragm. Upon the same principle, if a thin flaccid bladder, containing common air, be suspended in a jar of carbonic acid, it will become distended to the utmost by the entrance of the carbonic acid from without: or if the bladder distended with carbonic acid be suspended in the air, it will become flaccid, in consequence of the *exosmose* of the former prevailing over the *endosmose* of the latter.

It has been shown that gases flow into a vacuum with velocities which are inversely as the square roots of their densities; that is, with velocities corresponding to the numbers which express their diffusion-volumes: hence the law of diffusion has been regarded by Mr. T. S. Thomson (*Phil.*

Mag., 3rd series, iv. 321) as confirming Dalton's theory, that gases are inelastic towards each other; a conclusion, however, which Mr. Graham hesitates to adopt. (*Elements of Chemistry*, p. 75.)

In discussing the nature of flame and the causes of their luminosity and heat (p. 223,) I have alluded to the high temperature of that of hydrogen; it is occasionally employed for exciting intense heat; and, when mixed with oxygen, and burned as the mixture issues from a small jet, it excites a temperature nearly equal to that of the arc of flame in the voltaic circuit. A blow-pipe upon this construction was first made by Mr. Newman, and afterwards improved, as to its safety, by Professor Cumming, of Cambridge. (*Journal of Science and the Arts*, i. 65, and ii. 380.) A full account of the construction and use of this hydro-oxygen blow-pipe will be found in Dr. Clarke's book upon the subject. (London, 1819.) Mr. Hemming's safety-tube may also be used in these experiments. (See *Phil. Mag.*, 3rd series, i. 82.) An excellent mode of obtaining intense heat by the combustion of oxygen and hydrogen, consists in propelling them from separate air-holders through a burner composed of two concentric tubes: a good form of which has been contrived by Mr. Daniell. (*Phil. Mag.*, 3rd series, ii. 57.) The apparatus for this purpose has also been further improved by Mr. Maugham, especially as relates to its application to the solar microscope. (*Trans. Soc. Arts, &c.*, vol. L.)

HYDROGEN AND OXYGEN. WATER. PROTOXIDE OF HYDROGEN. ($h + o$)

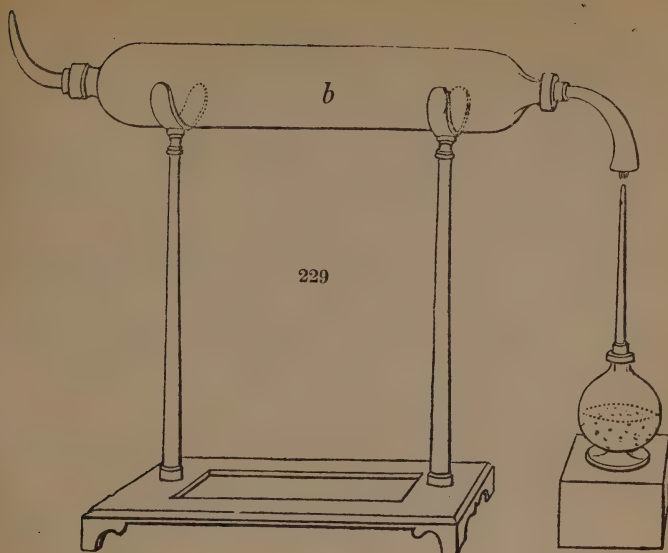
or q , or \dot{H} .—The discovery of the composition of water, one of the most important in the science of chemistry, was made by Cavendish, in 1788. (*Phil. Trans.*)

When *two volumes* of pure hydrogen gas are mixed with *one volume* of pure oxygen gas, and the mixture inflamed in a proper apparatus by the electric spark, the gases totally disappear, and water equal in weight to the gases consumed is formed: and again, if water be exposed to electrolytic action, it is resolved into *two volumes* of hydrogen, disengaged at the negative pole or cathode, and *one volume* of oxygen, disengaged at the positive pole or anode (see p. 302); so that water is thus proved by *synthesis*, and by *analysis*, to consist of two volumes of hydrogen, combined with one volume of oxygen. The specific gravity of hydrogen, compared with oxygen, is as 1 to 16; these numbers, therefore, represent the comparative weights of equal volumes of those gases; but as water consists of *one volume of hydrogen and half a volume of oxygen*, it is obvious that the relative *weights* of those elements will be as 1 : 8, or as follows:—

	Atoms.	Weights.	Per cent.	Volumes.
Hydrogen . . .	1 . . .	1 . . .	11.1 . . .	1.0
Oxygen . . .	1 . . .	8 . . .	88.9 . . .	0.5
Water . . .	1 . . .	9 . . .	100.0	

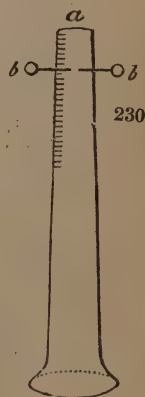
The experiments illustrating the composition of water, and showing the proportions in which its elements are united, may be divided into *synthetic* and *analytic*. Among these the following may be selected:—

Synthetic Experiments.—i. Burn a current of hydrogen under the copper funnel *a*, represented in the following wood-cut, fig. 229; by



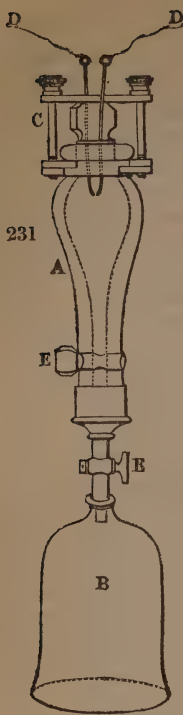
uniting with the oxygen of the atmosphere it will produce aqueous vapour, which passing into the glass cylinder *b*, will condense in drops*.

ii. If two measures of pure hydrogen be mixed with one of pure oxygen, and detonated in the graduated glass tube *a*, fig. 230, standing over water or mercury, by an electric spark passed through the platinum wires *b b*, the gases will entirely disappear. If there be any excess of either of the gases, the portion in excess will remain unconsumed. At the moment the explosion takes place the gaseous mixture becomes greatly expanded, probably to fifteen times its original bulk (DAVY on *Flame*, p. 90), and a portion is apt to escape at the bottom of the tube; hence the advantage of performing the experiment over mercury in the form of apparatus recommended by Dr. Ure. (See EUDIOMETER.)



iii. The same experiment may be thus varied. A (fig. 231) is a very strong and thick glass vessel provided with a glass stop-cock *E*, and with a ground stopper firmly secured by the brass collar *c*, through which the platinum wires *D D* pass. The vessel *A*, previously exhausted of air, is placed upon the bell-glass *B*, in the pneumatic trough, containing a mixture of pure oxygen and hydrogen in the above-mentioned proportions. Upon opening

* On examining the water thus produced, it is generally slightly acid from the presence of nitric acid, derived from the nitrogen in the atmosphere; if hydrogen be in excess it sometimes contains ammonia. (SAUSSURE, *Ann. de Chim.*, LXXI, p. 282.)



the stop-cocks *E F*, a quantity of the mixed gases passes into *A*, where, *after having carefully closed the stop-cocks*, it may be inflamed by an electric spark passed through the platinum wires. At the instant of the detonation, a vivid flame pervades the upper vessel, and it becomes lined with moisture. If the stop-cocks be again opened, a fresh portion of the mixed gases enters, and may be inflamed as before.

iv. A mixture of oxygen and hydrogen gases, suddenly submitted to violent mechanical compression, unite with combustion, and produce water. (BIOT.) Under a more gradual compression, equivalent to that of 50 atmospheres (by sinking the mixed gases in a tube, sealed by mercury, to a depth of 540 metres in the sea), the gases do not unite. (DELAROCHE.) Water may also be produced by heating the mixed gases to a temperature below that required for their combustion with flame. (DAVY on Flame, p. 68.) According to Grotthus, no explosion takes place in a mixture of two volumes of hydrogen and one of oxygen, expanded to six times its volume by heat, or to sixteen times its volume by diminished pressure. (*Ann. de Chim.* lxxxii.) Electric sparks, however, passed for some time through such a mixture, gradually produce water. A red heat, visible by day light, inflames the mixture;

but a very dull red heat only causes the combination of the gases without explosion. Mr. Graham states, that if a mixture of oxygen and hydrogen be heated in a vessel containing a quantity of pulverised glass, or any sharp powder, they begin to unite, in contact with the foreign body, in a gradual manner, without explosion, at a temperature not exceeding 660°.

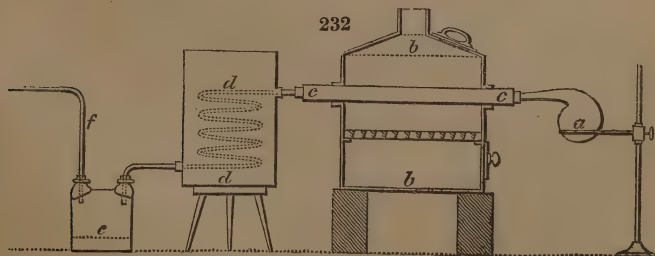
v. A very curious discovery connected with the present subject was made in the year 1824, by Professor Döbereiner, of Jena, who found that spongy platinum, (see PLATINUM,) possessed the singular property of causing the immediate combination of hydrogen and oxygen, with heat sufficient to inflame the gases, and of course to render the metal red-hot. If a small piece of well-prepared spongy platinum be held in a jet of hydrogen issuing from a small tube into the atmosphere, it immediately becomes hot enough to inflame the gas. If a mixture of oxygen and hydrogen, or of atmospheric air and hydrogen, not in explosive proportions, be submitted to the action of the platinum, it disposes the gases to slow combination, water is gradually formed, and if there be a sufficiency of oxygen, the whole of the hydrogen disappears under its influence; if, on the other hand, there be excess of hydrogen, the oxygen disappears. In analyzing certain gaseous mixtures, therefore, platinum, in this peculiar state of mechanical division, becomes a most valuable agent. For more convenient application to such purposes, the platinum may be mixed with an equal weight of pure clay, and moulded with a little water into small balls, which must be carefully dried at a high heat. These

may be conveniently thrown up into gases standing over mercury, and their power is not impaired by use; for they may always be rendered efficient, or their power restored, by heating them in the flame of a blow-pipe. Spongy platinum also causes the union of oxygen with several other gases, such as with carbonic oxide, and, at high temperatures, with olefiant gas; it also promotes the decomposition of nitric oxide by hydrogen. (DULONG and THENARD, *Ann de Chim. et Phys.*, xxiii. 440.) A very few other metals operate in the same way, but less perfectly than platinum, such as palladium and iridium. Gold and silver in fine leaves are efficient at temperatures above 212° .

vi. The extraordinary effects observed by Mr. Faraday respecting the action of the platinum which had formed the positive pole of the voltaic pile upon a mixture of oxygen and hydrogen gases, and which he has detailed and investigated in the sixth series of his *Experimental Researches in Electricity*, (*Phil. Trans.*, 1834, p. 55,) are apparently of the same nature as those observed by Döbereiner. He refers them to a peculiar attraction between the *perfectly clean* metallic surface and the particles of the gaseous mixture, resembling that by which bodies become *wetted* by fluids with which they do not combine chemically, or in which they do not dissolve; or the attraction which renders certain bodies hygrometric, though they neither dissolve in, nor combine with, water; or lastly, to a kind of attraction analogous to that between air and glass, so well known to barometer-makers. It may be conceived that by some such attractive force the particles of the oxygen and hydrogen become so approximated, and deprived of their gaseous repulsion, as to enter into chemical combination, and in so doing to evolve the heat which raises the temperature of the metal.

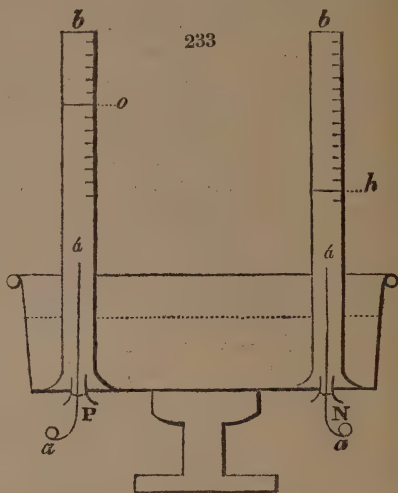
Analytic Experiments.—Water may be decomposed, or resolved into its elements, by a variety of processes, of which the following will suffice for our present illustration:—

i. *a* (fig. 232) is a glass retort, into which is introduced a given weight of water; *b b* a small furnace through which passes the porcelain tube *c c*, which terminates in the spiral pewter tube *d d*, immersed in water. A given weight of pure iron-wire, coiled up, is introduced into the tube *c*, and the whole made red-hot; the water in *a* is then made to boil, and the vapour, on coming into contact with the red-hot iron, is in part decomposed; the oxygen is retained by the iron; and the hydrogen, escaping through the tube *f*, may be collected as usual. Any undecomposed portion of water is condensed in the worm-pipe *d*, and drops



into the vessel *c*. After this experiment the iron will be found to have increased in weight; and if attention be paid to the quantity of water which has collected in *c*, and to the weight of the hydrogen gas evolved, it will be found that the weight gained by the iron, added to that of the hydrogen, will be equal to the weight of the water which has disappeared. Lavoisier concluded, from an experiment thus conducted, that water consisted of 85 parts by weight of oxygen, and 15 by weight of hydrogen: that is, that for every 15 grains of hydrogen gas evolved, 85 grains of oxygen were condensed by the iron.

ii. Decomposition by voltaic electricity best illustrates the composition of water, since it exhibits both the oxygen and hydrogen in the gaseous form. The annexed wood-cut represents a section of an apparatus for this purpose. It is a glass vessel containing water, having two wires of platinum, *a a*, passing through its bottom, which terminate in two narrow plates or strips of platinum, *a' a'*, which rise up into, and over which are inverted, the tubes *b b*, also filled with water. The wires are now connected with a moderately-powerful voltaic apparatus: oxygen is evolved at the positive, and hydrogen at the negative electrode, which gases rise into the tubes, and it is seen that one volume of oxygen, *o*, and two volumes of hydrogen, *h*, are the constant results*. If these gases be mixed and



* By passing electric discharges from a Leyden jar by two fine wires through water, oxygen and hydrogen are evolved at both; the decomposition therefore, is apparently not electropolar. In the electrolysis of water, as described in the text, the bubbles of hydrogen are larger and rise more regularly than those of oxygen, which are much more minute and diffused; a deficiency in the oxygen is also occasionally remarked, which, when the proportion of sulphuric acid added to improve the conducting power of the water exceeds that above mentioned, is sometimes considerable: it probably arises from the solution of a portion of the oxygen in the dilute acid, or from the formation of oxy-water. Mr. Faraday recommends for the Voltameter (p. 314), an acid of the specific gravity of 1.3. From a mixture of two measures of sulphuric acid and one

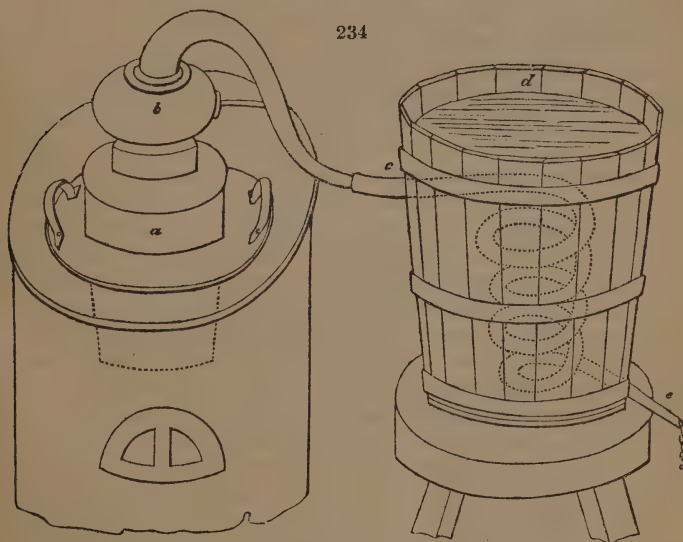
of water he obtained 42 volumes of hydrogen and only 12 (instead of 21) of oxygen. (*Researches*, vii., § 728.)

If the water used for voltaic decomposition be not perfectly pure, its impurities are shown by the production of acid and alkaline matter at the positive and negative pole. (See p. 306.) But pure water is so imperfect an electrolyte that, in the above experiment, it is convenient to render it more easy of decomposition by the addition of a little sulphuric acid. (See page 302, and note.) In using any apparatus, such as the voltameters, in which water is decomposed by platinum electrodes, care must be taken that no part of the clean electrode be exposed to the evolved gases, as it will tend to induce their recombination, and in so doing sometimes becomes red-hot and cause explosion.

detonated, pure water is again formed. In employing this apparatus the conducting power of the water requires to be augmented by the addition of about a tenth part of sulphuric acid.

Properties of Water.—Water, in its ordinary state, such as *spring* and *river water*, is always so far contaminated with foreign substances as to be unfit for many chemical purposes, and frequently, as will be more fully shown hereafter, even for domestic use. *Rain-water* is much more pure, but it always contains small quantities of carbonic acid and of atmospheric air, besides appreciable traces of vegetable or animal matter; to the latter it owes its property of becoming putrid when kept. Hassenfratz asserts that snow-water contains excess of oxygen.—(*Jour. de l'Ecole Polytech.*, cap. iv., 570.) Rain-water collected near the sea shows traces of chlorine. The distinction of water into *hard* and *soft* has reference to its less or greater purity. The impurities of water are

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separated by *distillation*, which process is usually conducted upon the large scale in a copper *boiler*, *a*, placed either in a portable furnace (fig. 234), or set in brickwork, according to its dimensions, to which is annexed the *still-head*, *b*, of the same material, or of pewter, connected with the pewter *worm* *c*, which is immersed in the *worm-tub*, or *refrigerator*, *d*, its lower end passing out at *e*. The water in this vessel must always be retained of a low temperature, to effect the condensation of the vapour in the spiral tube.

Distilled water, as commonly prepared, always affords minute traces of foreign matter, especially when subjected to Voltaic decomposition, and can only be considered as *perfectly* pure when re-distilled at a low temperature in silver vessels. (See page 308.)

Pure water is transparent, and without either colour, taste, or smell. It is a powerful refractor of light, and a very imperfect conductor of heat

(p. 156) and of electricity (p. 245). In consequence of the facility of obtaining it pure, it is assumed as a standard to which the relative weight of all other bodies may be compared, its specific gravity being called $= 1.000$; and hence the importance of estimating its weight with precision (p. 145). At the temperature of 62° , which is that to which specific gravities are usually referred, a cubic inch of water weighs 252.458 grains; or at 60° , the cubic inch weighs almost exactly 252.5 grains, and the cubic foot 998.217 ounces *avoirdupois*, which is so near 1000, that the specific gravity of any substance, in reference to water, is very nearly the absolute weight of one cubic foot of such substance in *avoirdupois* ounces. The specific gravity of gold for instance, is 19.3, in reference to water as unity, and, therefore, a cubic foot of gold weighs *nearly* 19300 ounces. Water is about 815 times heavier than atmospheric air. Water at mean temperature is also assumed as the unit to which the specific heats of bodies, especially of solids and liquids, are usually referred: the specific heat of water has been ascertained with much precision by Regnault. (*Ann. Ch. et Ph.*, LXXIII. 35.)

Water is susceptible of compression, as was originally shown by Canton. Perkins states that a pressure of 2000 atmospheres occasions a diminution of 1-12th its bulk (*Phil. Trans.*, 1820). This subject has been more recently examined into by Ørsted, whose results differ from those of Perkins: the estimate of the latter he thinks too great (*Edin. Jour. Science*, xii., 201). According to his experiments and those of Colladon and Sturm (*Ann. de Chim. et Phys.*, xxxvi., 140), its absolute diminution of bulk for each atmosphere is 51.3-millionths of its volume. It is stated by Dessaignes that when water is submitted to very sudden compression, it becomes luminous. (THENARD, *Traité de Chimie*, i. 432.)

At the temperature of 32° water congeals into ice, which, if slowly formed, produces needles crossing each other at angles of 60° and 120° . Their forms are various, but the primitive figure has not been ascertained, though it is probably rhomboidal. The specific gravity of ice is 0.94, or thereabouts, varying a little in consequence of the air-bubbles which it includes: the densest ice, however, obtained by freezing-water deprived of air, is always lighter than water. Ice is a non-conductor of electricity, and under favourable circumstances becomes electric by friction. It is a very bad conductor of heat. In freezing, the water expands with such force as to burst very thick and strong vessels in which it is confined. The rupture of iron and leaden pipes is a familiar instance of this power. The most interesting experiments upon the subject are those of Major Williams (*Edin. Phil. Trans.*, vol. ii.) Bomb-shells, about 13 inches in diameter, and more than 2 inches thick, were filled with water; the fuse-holes were then plugged with iron-bolts, and, thus charged, were exposed to the open air at a temperature between -4° and -19° . At the moment of congelation the plugs were thrown out, and the ice protruded through the fuse-hole. When the plug was duly secured, the shell itself burst. The greatest difference observed in these experiments between the bulk of water before and after congelation was : 174 : 184. Exposed to the air, ice loses considerably in weight by evaporation. Hail is always crystallized in the form of two six-sided pyramids, applied base to base. The faces of the two pyramids meet at angles of about

80°, and one of the pyramids is always truncated. (SMITHSON, *Ann. of Phil.*, 2nd series, v. 340.)

If water be exposed to heat in open vessels it boils, or is converted into steam, at 212°, the barometer being at 30 inches; but the boiling-point of water varies considerably with the pressure (p. 173). The specific gravity of air being considered as = 1; that of *steam* is 0·624; 100 cubical inches weighing, at the temperature of 212°, and under mean pressure, 14·96 grains.

In the constitution of aqueous vapour or steam, *two* volumes of hydrogen and *one* of oxygen are condensed into *two* volumes, as in the annexed diagram. The specific gravity, therefore, of steam compared with that of hydrogen, is as 9 to 1: or in reference to air as = 1,

Hydrogen. 1	Oxygen. 8	=	Steam. 9
----------------	--------------	---	-------------

1 volume of hydrogen, specific gravity	0·0694
$\frac{1}{2}$.. oxygen,	0·5555

Specific gravity of steam therefore = 0·6249

At mean pressure, and at the temperature of 212°, the bulk of steam is 1689 times that of water. (See p. 172.)

Water enters into combination with a variety of substances, and is retained with various degrees of force: where it contributes to the regular form and transparency of crystallized bodies, it is termed *water of crystallization*. In other cases the compounds which water forms with substances are called *hydrates*, as with many of the metallic oxides; in both cases it may be considered as one of the constituents of the bodies, for it exists in them in a definite proportion.

Water, which has been exposed to the atmosphere, always contains a portion of air, as may be proved by boiling it, or by exposing it under the exhausted receiver of the air-pump. To separate the air, the water must be boiled for about two hours. It absorbs oxygen gas in preference to atmospheric air or nitrogen, and, when the air is expelled by boiling, the last portions contain more oxygen than those first given off. (HUMBOLDT and GAY LUSSAC, *Journal de Physique*, 1805.) It is by the oxygen thus dissolved in water that the blood of fishes is aerated, and as at great altitudes the quantity of the air in water is very small, in consequence of diminished pressure, it is found that fishes never thrive in alpine lakes.

Mr. Dalton states, that 100 cubical inches of spring water afford about two inches of air, which, after losing from 5 to 10 per cent. of carbonic acid by the action of lime-water, consists of 38 per cent. oxygen and 62 nitrogen (*New System*, 271). Dr. Henry obtained 4·76 cubic inches of gas from 100 of the water of a deep spring, of which 3·38 were carbonic acid gas, and 1·38 air, of the same standard as that of the atmosphere. There can, however, be no doubt, that the aeriform contents of different springs vary both in quantity and quality.

The following Table exhibits the quantity of different gases which water is capable of absorbing at mean temperature and pressure, the water being previously deprived of all aeriform matter by long boiling.

GASES.	100 Volumes of Water absorb	AUTHORITY.
Oxygen	3·7 volumes	Dalton.
Chlorine	200	Gay Lussac.
Oxide of Chlorine	800	Stadion.
Hydrogen	1·56	Henry.
Hydrochloric acid	50000 average	Davy.
Hydriodic acid		
Nitrogen	1·56	Henry.
Nitrous oxide	100	Ditto
Nitric oxide	5	
Nitrous acid		
Ammonia	67000 average	
Sulphurous acid	3000	Davy.
Sulphuretted hydrogen	100	Dalton.
Hydroguret of phosphorus	2·14	Henry.
Bi-hydroguret of phosphorus	12	Davy.
Carbonic oxide	2 average	
Carbonic acid	100	Dalton.
Carburetted hydrogen	12·5	Dalton.
Cyanogen	450	Gay Lussac.
Fluoboric acid	70000	John Davy.
Fluosilicic acid	35000	Saussure.
Hydroselenic acid	300	Berzelius.

The great importance of water as a natural and artificial agent, both mechanical and chemical, must be sufficiently obvious. The manner in which its changes of state or form influence the temperature of the globe, will be evident by a reference to the details given in the section on heat. When it freezes, the expansion which it suffers, and the force with which its particles arrange themselves in the crystalline form, are often actively concerned in the disintegration and decay of rocks and strata, and in the production of soils. Water is a most general and useful solvent, especially of saline bodies, the relative solubilities of which will be stated under their individual chemical history. Considered as a chemical agent, it is frequently resolved into its elements; these are sometimes respectively concerned in the production of new compounds: when chloride of phosphorus, for instance, acts upon water, its chlorine combines with the hydrogen of the water to form hydrochloric acid, and the phosphorus and oxygen unite to form phosphoric acid. In other cases bodies decompose water by the absorption of oxygen only, and the hydrogen is liberated in the gaseous form; but there is no instance in which the hydrogen is absorbed, so as to cause the evolution of gaseous oxygen.

PEROXIDE OF HYDROGEN.—OXYGENATED WATER. ($\text{h} + 2\text{o}$) or H_2O_2 . This singular compound was discovered by Thenard, in 1818: he obtained it by dissolving the *peroxide of barium* in hydrochloric acid and water, and adding sulphuric acid, by which the *protoxide* of barium is precipitated in the state of sulphate, and the excess of oxygen transferred to the water: by several repetitions of this process the water is gradually saturated with oxygen. There are so many difficulties attending the whole process, that it has been seldom repeated, and we know little of the nature of this extraordinary compound, except through the original essays of its discoverer: it has been surmised, from its properties, and

mode of formation, that it may be an aqueous solution of liquid oxygen; Thenard, however, regards it as a definite combination of hydrogen and oxygen, in which one atom of the former is combined with two of the latter, as follows:—

				Thenard.	Volumes.
Hydrogen 1 1 5.9 6.02 1
Oxygen 2 16 94.1 93.98 1
Peroxide of Hydrogen	1	17	100.0	100.00	

Much of the success of the process for obtaining this compound depends upon the purity of the peroxide of barium: the following details are from Thenard's memoir, (*Ann. de Chim. et Phys.*, viii. ix. x. and L.; THENARD'S *Traité de Chim.*, Ed. 4, ii., p. 41.)

To obtain pure peroxide of barium, prepare a pure nitrate of baryta, and give it a strong heat in a porcelain vessel, by which, baryta, not quite pure, but containing traces of silica and alumina but no manganese, will be obtained; the latter impurity must always be most cautiously avoided, for oxide of manganese possesses the property of energetically decomposing the oxygenated water. The baryta, broken into small pieces, is then introduced into a luted glass tube (the glass should not contain lead) large enough to contain about two pounds of it, and being heated to dull redness, a current of dry and perfectly pure oxygen gas is passed through it, which it rapidly absorbs; this operation is to be continued till the oxygen escapes from a small tube inserted into the opposite extremity of the larger one. The *peroxide of barium* thus obtained is pale gray, and frequently some pieces are speckled with green, which announces the presence of manganese, and which should be rejected: its distinctive character is, that it crumbles when a few drops of water are added to it, without producing heat.

The process then proceeds as follows. Take a certain quantity of water (about eight ounces for instance), and add to it a sufficiency of pure and fuming hydrochloric acid to dissolve about 230 grains of baryta: put this acid liquor into a glass vessel, which, during the operation, must be surrounded by ice: then take about 185 grains of the peroxide, rub it into a fine paste with a little water in an agate mortar, and put it into the acid liquor with a box-wood spatula; it soon dissolves without effervescence: to this solution add pure sulphuric acid, drop by drop, stirring it with a glass rod, till it is in slight excess, which is known by the readiness with which the sulphate of baryta falls: then dissolve a second portion of the peroxide and precipitate as before, taking care to use enough, but not too much, sulphuric acid. The liquor is now to be filtered, and the residue washed with a little water, so as to keep up the original measure by adding it to the first portion: a second and third washing of the residue with very small quantities of water may be advisable, and these liquors should be kept apart for the purpose of washing the filters in subsequent operations.

A fresh portion of the peroxide is then dissolved in the filtrated liquor and decomposed as before, filtering at every two operations, and washing the filter with the savings of the others; we thus proceed till the water is sufficiently oxygenated. When about two pounds of the

peroxide have been consumed, the water will be united to about thirty times its volume of oxygen, which is as much as it will retain, unless some hydrochloric acid be added, in which case M. Thenard has made it retain 125 volumes.

When the water is sufficiently oxygenated, it is retained in the ice, and supersaturated with the peroxide of barium, which occasions the separation of flocculi of silica and alumina, coloured with a little oxide of iron and of manganese; the whole is then filtered as quickly as possible, and returned into the vessel surrounded by ice; the baryta is separated by sulphuric acid; and pure sulphate of silver is added, to separate the hydrochloric acid, upon which the liquid, before milky, becomes suddenly clear. The sulphuric acid is ultimately separated by baryta, the liquor filtered, and placed in a shallow vessel, under the air-pump receiver, including a basin of sulphuric acid; the receiver being exhausted, the water evaporates and is absorbed by the acid, while the *peroxide of hydrogen*, being less vaporisable, remains: if it give out any oxygen, which sometimes happens, from its containing impurities, a drop or two of weak sulphuric acid will prevent its further evolution.

The peroxide of hydrogen thus concentrated has the following properties: its specific gravity is 1.45; it is colourless and inodorous; it blisters the cuticle of the tongue, and has a peculiar metallic taste. It does not congeal when exposed to cold, unless diluted. It is rapidly decomposed at a heat below 212° , and very slowly at ordinary temperatures; it may be long kept at 32° . It is decomposed by the voltaic pile with the same phenomena as water. It is decomposed by all metals except iron, tin, antimony, and tellurium: the metals should be finely divided, or in powder: silver and oxide of silver decompose it very suddenly with the evolution of heat and light: platinum and gold produce the same phenomena; lead and mercury slowly separate the oxygen. Orpiment and powdered sulphuret of molybdenum act upon it with the same violence as silver; the peroxides of manganese and of lead also occasion its instant decomposition.

HYDROGEN AND CHLORINE. HYDROCHLORIC ACID. MURIATIC ACID. CHLORHYDRIC ACID* ($h + c$) or hc' , or H Cl.—When equal volumes of hydrogen and chlorine are mixed, and exposed to light, they slowly combine, and produce *hydrochloric acid gas*. If the above mixture be exposed to the direct solar rays, a detonation often ensues, as was first remarked by Gay Lussac and Thenard.—(*Recherches Physico-Chymiques*, ii. 129.) It also detonates when suddenly exposed to the intense light

* This is a *hydrogen-acid*, or *hydracid*, of which there are several; some with simple, others with compound bases; chlorine, iodine, bromine, and fluorine, form with hydrogen acids analogous to the hydrochloric, and these constitute an important and well-defined group; sulphur, selenium, arsenic, tellurium, phosphorus, and a few other substances, form a second group; and a third includes the hydracids with compound

bases, such as the hydrocyanic, &c. The hydracids do not combine with basic oxides to produce salts, but when they act on such oxides, a mutual decomposition of the oxide and of the acid ensues: thus when soda or oxide of sodium is added to hydrochloric acid, the sodium of the base and the chlorine of the acid unite to form chloride of sodium, and the oxygen of the base and the hydrogen of the acid form water.

of the voltaic discharge passing between charcoal points. That direct solar light is not necessary to effect this combination has been shown by Professor Silliman (*American Journal of Science*, iii. 342), who relates a case of the explosion of the mixed gases in dull and cloudy daylight. This fact furnishes a caution against mixing any considerable quantities of chlorine and hydrogen. According to Dr. Henry, the agency of light on these gases may be beautifully shown by filling a tube, about half an inch diameter, and twelve inches long, with the mixed gases, and alternately shading it with an opaque cover, and exposing it to the sun's rays. The moment the tube is exposed even to the diffused light of day, a cloudiness will appear within it, and the water will ascend more or less rapidly according to the intensity of the light. The effect even of a passing cloud is distinctly seen in retarding the rapidity of the combination, which is very striking in the full solar light.—(*Elements*, vol. i.) Seebeck states that the mixed gases, exposed to the sun's rays in a tube of violet-coloured glass, combine rapidly, but without explosion, and that in a tube of red glass they scarcely act upon each other.

The best mode of showing the composition of hydrochloric acid, is to introduce into a small but strong glass vessel a mixture of the two gases, and to inflame them by the electric spark; no change of volume ensues, and muriatic gas results. The apparatus shown at fig. 230, may be used for this purpose; or a jet of hydrogen may be inflamed and introduced into a jar of chlorine; during its combustion the yellow colour of the chlorine disappears, and hydrochloric acid is formed.

Sir H. Davy found that the heat evolved during the combustion of a mixture of equal volumes of chlorine and hydrogen exceeded that produced by a mixture of oxygen and hydrogen, and that the former mixture was inflamed at a lower temperature, and would bear much greater rarefaction than the latter, without losing its explosive property. Oxygen and hydrogen ceased to explode when rarefied 18 times, but chlorine and hydrogen retain their combustibility when rarefied 24 times.

By passing a succession of electric sparks through hydrochloric acid gas Dr. Henry effected its partial decomposition, and when it had gone to a certain extent, the gases again combined: he also found, that by passing a mixture of oxygen and hydrochloric acid gas through a red hot porcelain tube, or by the transmission of electric sparks, water was formed and chlorine evolved. At the temperature of 250° , the same change was produced upon the mixture by spongy platinum.—(*Phil. Trans.*, 1812 and 1824.)

Hydrochloric acid gas may also be decomposed by the action of several of the metals.—(DAVY, *Phil. Trans.*, 1810.) Potassium, for instance, absorbs the chlorine, and the hydrogen is evolved. This experiment is best made by introducing a piece of potassium into a small retort, which is then to be exhausted and filled with hydrochloric acid gas from a jar standing over mercury. The potassium generally takes fire, but is sometimes prevented burning by the formation of a film of chloride of potassium, and then requires to be heated, which, however, should be done carefully, as the retort is apt to break in consequence of the intensity of the combustion that ensues. When it has cooled it will be found that the residuary gas is *hydrogen*, equal to half the original bulk of the

hydrochloric acid. If a piece of burning potassium be introduced in a small copper spoon, into a bottle filled with hydrochloric acid gas, the metal continues in vivid combustion, and the evolved hydrogen at the same time takes fire, and burns with flame at the neck of the bottle. Tin and lead heated in the gas also effect its decomposition, and

Hydrogen.	Chlorine.	=	Hydrochloric Acid.
1	36		37

evolve exactly half its bulk of hydrogen. The specific gravity of hydrogen to chlorine is as 1 to 36; one volume of hydrogen and one

of chlorine combine to form two volumes of hydrochloric acid gas, as shown in the above diagram; or (according to Davy, and to Gay Lussac and Thenard), hydrochloric acid gas consists of

					Volumes.
Hydrogen	..	1	..	1	2.7
Chlorine	..	1	..	36	97.3
<hr/>					<hr/>
Hydrochloric acid		1		37	100.0
					<hr/>
					2

The greater number of metallic oxides when heated in gaseous hydrochloric acid, decompose it; metallic *chlorides* are formed, and the oxygen of the oxide combining with the hydrogen of the acid forms water.

Hydrochloric acid gas was discovered by Priestley in 1772: it is generally procured for the purposes of experiment, either by applying heat to the strong liquid hydrochloric acid; or, more readily and in greater abundance, by acting upon common salt, or sal-ammoniac, by sulphuric acid; the evolved gas must be received over mercury. The salt should be put in fragments into a small tubulated retort, which may be one-fourth filled with it: the sulphuric acid should barely cover the pieces of salt; the gas is instantly extricated, and when its evolution slackens, it may be quickened by the gentle heat of a lamp. It is convenient to put a long strip of folded blotting-paper into the neck of the retort, which absorbs any liquid that may chance to go over, and prevents its soiling the mercury. With a little practical dexterity, clean and dry bottles may be conveniently filled with this gas in the way described in the note at page 366.

The specific gravity of hydrochloric acid gas compared with air is 1.269; and as it consists of equal volumes of hydrogen and chlorine (combined without change of volume), 100 cubical inches must weigh 39.36 grains; for

50 cubic inches of hydrogen	weigh	1.069
50 .. chlorine	..	38.299
<hr/>		<hr/>
100 .. hydrochloric acid gas	..	39.368

According to Thomson, 100 C. I. at 32° weigh 42.126 grains.

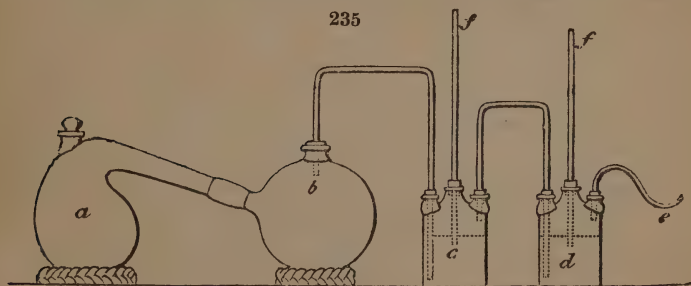
Although permanently gaseous at all common temperatures and pressures, Mr. Faraday liquified this gas by generating it in a sealed tube, so as to expose it to a pressure of about 40 atmospheres at 50°. It was colourless, and possessed a refractive power inferior to that of water.

Hydrochloric acid gas is perfectly unrespirable; it extinguishes the flame of a taper, and is itself unflammable. It irritates the skin. It

has a strong attraction for water: when it escapes into the air it forms visible fumes, arising from its combination with aerial vapour. A piece of ice let up into the gas over mercury, immediately liquifies and absorbs it: and if a tall jar of the gas be carefully transferred, with its mouth downwards, from the mercurial to the water-trough, the water instantly rushes in with violence, and fills it. Litmus-paper is powerfully reddened by this gas, and turmeric-paper receives from it a brown discoloration not unlike the effect of an alkali.

Water takes up 480 or 500 times its bulk of hydrochloric acid gas, and has its specific gravity increased from 1 to 1.210. This may be shown by throwing up a few drops of water into a tall jar of the gas standing over mercury; the gas disappears, and the mercury fills the vessel. There is considerable elevation of temperature during this condensation of the gas.

For saturating any quantity of water with gases which are easily soluble in that fluid, we generally employ *Woulfe's apparatus*, one form of which is shown in the annexed cut. *a* is a tubulated retort, in which



the materials producing the gas or vapour are contained; *b*, a receiver, communicating by a bent tube with the three-necked bottle *c*, which is connected also by a tube with *d*. These bottles are about half-filled with water, or any other fluid intended to be saturated with the gas; when that in *c* has become saturated, it passes into *d*, and afterwards through the tube *e*, which may be placed under the water, or mercury, in the pneumatic trough. In case absorption should take place in the vessels *a* or *b*, the pressure of the external air might force the water from *d* into *c*, and from *c* into the balloon *b*. This is prevented by the safety-tubes *f, f*, which, dipping not more than half an inch under the surface of the water, allow a little air to enter, so as to compensate for the absorption. The different joints may be secured either by grinding, or by well-cut corks rendered tight by a mixture of drying-oil and pipe-clay.

When gaseous hydrochloric acid is thus dissolved in water, it forms the *liquid hydrochloric acid*, commonly called *muratic acid*, or *spirit of salt*, which was discovered by Glauber about the middle of the seventeenth century. It is generally procured by distilling a mixture of dilute sulphuric acid and common salt. The proportions directed in the *London Pharmacopœia* are two pounds of salt, and 20 ounces of sulphuric acid, diluted with 12 ounces of water. The retort containing these ingredients may be luted on to a receiver, containing

the same quantity of water used in diluting the sulphuric acid, and the distillation carried on in a sand-bath. The specific gravity of the product is stated to be 1.160, and 100 grains of it should be saturated by 132 grains of crystallized carbonate of soda. The quantity of real acid in hydrochloric acid of different densities is best ascertained by the quantity of pure carbonate of lime (Carrara marble, for instance), which a given weight of the acid dissolves. Every 50 grains of the carbonate are equivalent to 37 of real acid.

In preparing this acid upon the large scale an apparatus of earthenware is sometimes used, similar to that described under the article *Nitric Acid*; the market, however, might easily be supplied with hydrochloric acid to any amount, were the demands adequate; for in the operations in which common salt is decomposed for the manufacture of carbonate of soda, enormous quantities of hydrochloric acid are thrown away.

When this acid is pure, it is perfectly colourless, but it generally has a yellow hue arising from particles of cork or lute that have accidentally fallen into it, or sometimes from a little iron. Dr. Thomson suggests that the pale yellow tint occasionally observed in this acid apparently pure, may possibly arise from a trace of bromine, derived from the salt. The acid of commerce almost always contains iron and sulphuric acid, and sometimes nitric and sulphurous acid. The iron may be detected by the black tint produced by tincture of galls, in the acid previously saturated by carbonate of soda. If a dilute solution of chloride of barium, dropped into the acid, occasion a white cloud or precipitate, it announces sulphuric acid. The presence of nitric acid (and of free chlorine and bromine?) is shown by boiling some gold-leaf in the suspected hydrochloric acid, and then dropping into it a solution of protochloride of tin, which, if nitric acid were present, produces a purplish tint, showing the gold to have been acted upon, which it is not by pure hydrochloric acid. Sulphurous acid is indicated by the addition of a few crystals of protochloride of tin, which, after standing, produces a brown precipitate, containing sulphur in combination with tin (GERARDIN). Saline substances may be detected by evaporating the acid to dryness: when pure, it leaves no residue.

The highly-concentrated liquid acid emits copious fumes when exposed to air: it boils at a temperature of about 112° *, and gives off the gaseous acid: it freezes at -60° . When mixed with water, it occasions a slight elevation of temperature. It is decomposed by many substances containing loosely-combined oxygen, such as chloric, iodic, and bromic acids, and several of the metallic peroxides. Its decomposition by peroxide of

* The variation of the boiling-point with the density of hydrochloric acid is shown in the following table by Dalton, from which it appears that it is highest when it contains between 19 and 20 per cent. of the gas: the strong acid becoming weaker, and the weak acid stronger by boiling.

Sp. Gr.	Boil. pt.	Sp. Gr.	Boil. pt.	Sp. Gr.	Boil. pt.
1.166	170°	1.121	228°	1.035	219°
1.154	190	1.094	232	1.018	216
1.144	212	1.075	228	1.009	214
1.136	217	1.064	225		
1.127	222	1.047	222		

manganese, for the production of gaseous chlorine, has already been referred to: in this case, oxygen is imparted by the oxide to the hydrogen of the acid, so as to form water, and the chlorine previously in combination with the hydrogen is liberated; at the same time a chloride of manganese is formed. In this case, 1 atom of peroxide of manganese, and 2 atoms of hydrochloric acid, give rise to the production of 2 atoms of water and 1 atom of chloride of manganese, 1 atom of chlorine being evolved. The elements which are employed are

1 atom Manganese . . = 28	2 atoms Hydrogen . . . = 2
2 atoms Oxygen . . . = 16	2 „ Chlorine = 72
<hr/>	
1 atom Peroxide of } = 44	2 „ Hydrochloric } = 74
Manganese . . }	acid . . . }

The products of their mutual reaction are

1 atom Manganese . . = 28	2 atoms Hydrogen . . . = 2
1 „ Chlorine . . . = 36	2 „ Oxygen = 16
<hr/>	
1 „ Chloride of } = 64	2 „ Water = 18
Manganese . . }	
1 atom Chlorine = 36.	

or, in symbols, $(man + 2o)$ and $2(h + c) = (man + c) 2(h + o)$ and c .

The decomposition of hydrochloric by nitric acid will be afterwards explained. When metallic zinc is put into strong liquid hydrochloric acid it is rapidly decomposed, and the *hydrogen* copiously evolved may be burned as it escapes: some peroxide of lead added to another portion of the acid immediately disengages *chlorine*, which may be shown by its bleaching power upon a piece of paper dipped in indigo blue: this experiment well illustrates the separation of the two elements of the acid. In the voltaic circuit its chlorine is evolved at the anode and its hydrogen at the cathode, so that when thus electrolysed, and tinged with indigo, a bleaching effect is produced at the anode (p. 311).

Uncombined hydrochloric acid exists in small quantity in the human gastric juice; it is not found in nature except as an occasional volcanic product. The principal uses of this acid are as a medicine, and in some of the arts, where it is chiefly employed as a solvent of metals. It has been used in the gaseous state as a disinfectant, but is more annoying, and less efficient than chlorine; indeed, by some, its disinfecting powers have been altogether denied. It is extremely injurious to vegetation: mixed with 20,000 times its volume of atmospheric air it proves fatal to plants, shrivelling and killing all the leaves in twenty-four hours. (CHRISTISON and TURNER.)

The following tables by Mr. E. Davy and by Dr. Thomson show the value and atomic composition of hydrochloric acid of different densities: Dr. Ure, in his *Dictionary*, has also published a valuable and extended table upon the same subject; the data upon which it is formed and several important facts connected with this subject, will be found in his paper relating to it in the *Quarterly Journal of Science* (xii. 286).

(Temp. 40° Fah. Bar. 30.)

Specific Gravity.	100 Grains contain of Hydrochloric Gas.
1·21	42·43
1·20	40·80
1·19	38·38
1·18	36·36
1·17	34·34
1·16	32·32
1·15	30·30
1·14	28·28
1·13	26·26
1·12	24·24
1·11	22·30
1·10	20·20
1·09	18·18
1·08	16·16
1·07	14·14
1·06	12·12
1·05	10·10
1·04	8·08
1·03	6·06
1·02	4·04
1·01	2·02

Atoms of Water to 1 of Acid.	Real Acid in 100 of the Liquid.	Specific Gravity.
6	40·66	1·203
7	37·00	1·179
8	33·95	1·162
9	31·35	1·149
10	29·13	1·139
11	27·21	1·128
12	25·52	1·119
13	24·03	1·112
14	22·70	1·106
15	21·51	1·100
16	20·44	1·096
17	19·47	1·090
18	18·59	1·086
19	17·79	1·082
20	17·05	1·078

It appears from Dr. Thomson's table that the strongest liquid hydrochloric acid contains 1 atom of real acid + 6 atoms of water; when this is evaporated in the air, acid escapes, and it comes, according to Graham, to contain 1 atom of acid + 12 of water; according to Dr. Clark, the acid which is unaltered by distillation contains about 16 atoms of water.

HYDROGEN AND IODINE; HYDRIODIC ACID. ($h+i$) or hi or $H\ I$.—This compound of hydrogen and iodine was first examined by Davy and Gay Lussac. (*Phil. Trans.*, 1814. *Ann. de Chim.*, xci.) It cannot be obtained by the action of sulphuric acid upon iodide of sodium or potassium, because the hydriodic and sulphuric acids partially decompose each other, evolving iodine, and forming sulphurous acid and water. Hydriodic acid may be formed by the direct union of its elements, as by passing a mixture of hydrogen and the vapour of iodine through a red-hot tube; but it is most easily procured by the mutual action of water, phosphorus, and iodine; or, what amounts to the same thing, by the action of iodide of phosphorus on water. In thus procuring it, it is convenient to use a retort tube, into the bulb of which is introduced the moist iodine, and a small stick of phosphorus, about a tenth part of the weight of the iodine, placed in the neck above it, which can be shaken down upon the iodine when the beak of the tube or retort is placed under the inverted jar; a quantity of the gas is instantly generated, and a further portion is obtained on applying the flame of a spirit-lamp. In this case decomposition of the water and of the iodide ensue, and phosphorus and hydriodic acids are the results. Upon the same principle it may be obtained by previously preparing iodide of phosphorus, and gently heating it with a little water: if too high a temperature be used, phosphuretted hydrogen is also given off.

According to D'Arcet, hydriodic acid gas may be obtained very pure by the following process:—Hydrophosphoros acid is to be evaporated

until upon the point of evolving phosphuretted hydrogen gas. It is then to be put, with its weight of iodine, into a small tube retort; the gas is liberated, upon applying a gentle heat: 100 grains of the acid, and 100 of iodine, afforded 120 cubical inches. The residue of the operation is a mixture of phosphoric acid, and of the compound of hydriodic acid and phosphuretted hydrogen. (*Ann. de Ch. et Ph.*, xxxvii. 220.)

Whichever process is followed, if the gas be received over mercury it should be transferred as fast as possible into an exhausted vessel, as it is otherwise soon decomposed. It may often be conveniently collected in dry phials, without a mercurial trough, by its density, as in the methods described in the note to p. 230.

Hydriodic acid is colourless, sour, exhales fumes in the air, and smells like hydrochloric acid. It strongly reddens vegetable blues. Its specific gravity compared with air is as 4.38 to 1; 100 cubic inches weighing about 136 grains (or 142.4 grains at the temperature of 32°. THOMSON). Compared with hydrogen its specific gravity is as 63.5 to 1. It is not permanent at a red heat, for when passed through a red hot porcelain tube it is partially resolved into iodine and hydrogen.

Hydriodic gas is rapidly and abundantly absorbed by water, but in what exact proportion has not been determined. The solution, exposed to a temperature below 260°, becomes concentrated by loss of water; at about 260° it boils, and may be distilled. The specific gravity of the strongest liquid acid is 1.7. It becomes dark-coloured when kept in contact with air, in consequence of a partial decomposition, and it readily dissolves iodine, becoming of a deep brown colour. It is decomposed by chlorine and by nitric and sulphuric acids.

The *liquid hydriodic acid* is best prepared by passing sulphuretted hydrogen through a mixture of iodine and water: sulphur is deposited, and on heating and filtering the liquor, a pure solution of hydriodic acid is obtained, which may be concentrated by evaporation. It may also be obtained by heating iodine, phosphorus, and water: or by passing sulphuretted hydrogen through a solution of 1 part of iodine in 16 of alcohol, filtering, diluting with 32 of water, and subsequent distillation to drive off the alcohol and excess of sulphuretted hydrogen.

When hydriodic acid gas is mixed with oxygen, and passed through a red-hot tube, it is resolved into iodine and water. Its decomposition by chlorine produces hydrochloric acid, sometimes with explosion, and the blue vapour of iodine is rendered evident, but presently disappears in consequence of the formation of chloride of iodine. This decomposition is beautifully shown by suffering hydriodic acid gas to pass into a jar of atmospheric air, mixed with about a twelfth its bulk of chlorine; the violet fumes are then more permanent. A little strong nitric acid dropped into hydriodic acid gas energetically decomposes it, with the evolution of so much heat that the gas is occasionally inflamed. (TURNER.)

The experiments of Gay Lussac have proved the composition of hydriodic acid gas to be analogous to that of the hydrochloric: namely, that it consists of 1 volume of the vapour of iodine, and 1 of hydrogen: these produce 2 volumes of the acid. By the action, for instance, of mercury and some other metals, hydriodic acid gas is decomposed, the iodine being absorbed by the metal, and evolving from 2 volumes of the

gas, 1 of hydrogen: so that the annexed diagram represents its composition. That such is the composition of this acid is also shown by its weight, for,

Hydrogen	Iodine.	Hydriodic Acid.
1	126	127

	50 cubic inches of hydrogen weigh	50 " " iodine vapour	100 " " hydriodic gas	Gras.
				1.06
				134.92
				135.98

Or, it consists of

	Hydrogen	Iodine	Hydriodic acid	Volumes.	Sp. Gr.
	1	126	1	0.8	0.069
	1	126	1	99.2	8.700
	1	127	100.0	2	4.384

Hydriodic acid dissolves iodine; so likewise do the solutions of iodide of potassium and of zinc; taking up a quantity of iodine equal to that which they already contain: these compounds have been termed *ioduretted iodides*, and are by some considered as containing a peculiar acid which may be termed *hydriodous* acid, composed of 1 atom of hydrogen = 1 + 2 of iodine = $126 \times 2 = 252$.

The hydriodic acid is not found uncombined in nature; some of its combinations have already been mentioned under the head of *iodine*. Its presence may be detected by mixing a cold solution of starch with the liquid suspected to contain it, and then adding a few drops of a solution of chlorine or of nitric or sulphuric acid: this liberates iodine, and produces a blue tint.

HYDROGEN AND BROMINE. HYDROBROMIC ACID. ($h+b$) or hb' or HBr . Bromine and hydrogen do not act upon each other, even under the influence of the sun's rays, at common temperatures; but when bromine, phosphorus, and water, are brought into contact, a decomposition ensues analogous to that described under the article *hydriodic acid*; and *hydrobromic gas* is generated, which may be collected over mercury, or in dry phials. Hydrobromic gas may also be obtained by acting upon a mixture of bromine vapour and hydrogen by a coil of red-hot platinum wire: and it is evolved when bromide of potassium is decomposed by sulphuric acid, but in this case a portion of it is apt to be decomposed.

This gas is colourless, sour, of a pungent and highly-irritating odour, and yields dense vapours when mixed with humid air. It undergoes no change when passed through a red-hot tube, either alone or mixed with oxygen or iodine; but chlorine decomposes it, producing vapour and drops of bromine, which, being absorbed by mercury, leaves hydrochloric acid. We learn, therefore, that the attraction of bromine for hydrogen exceeds that of iodine, but is inferior to that of chlorine. The attraction of oxygen, and of bromine for hydrogen, is probably nearly equal; for bromine does not decompose water, nor does oxygen decompose hydrobromic acid. Hydrobromic gas is not altered by mercury, but tin and potassium entirely decompose it; the former requires the aid of heat;

but potassium acts at common temperatures, diminishing the gas to half its bulk, and becoming converted into a bromide of potassium. Hence it appears that the constitution of hydrobromic acid is analogous to hydrochloric and hydriodic acids, and that it consists of equal volumes of hydrogen and bromine vapour. The weight therefore of 100 cubic inches of hydrobromic acid will be as follows:—

Hydrogen.	Bromine.		Hydrobromic Acid.
1	78	=	79

50 cubic inches of hydrogen weigh	1.06	Grs.
50 " " bromine vapour	84.00	
100 " " hydrobromic gas	85.06	

Or, it consists of

			Volumes.	Sp. Gr.
Hydrogen	1 . . . 1 . . .	1.266 . . . 1 . . .	1 . . .	0.069
Bromine	1 . . . 78 . . .	98.734 . . . 1 . . .	1 . . .	5.400
Hydrobromic acid 1	79	100.000	2	2.734

Hydrobromic acid gas is rapidly absorbed by water; heat is evolved, and a fuming liquid acid obtained, which is colourless when pure, but which readily dissolves bromine, and acquires a yellow colour. This acid may also be obtained by the action of sulphuretted hydrogen on bromine and water. It is instantly decomposed and discoloured by chlorine. Nitric acid also decomposes it, producing the evolution of bromine, and the formation of water and nitrous acid. This mixture dissolves gold. Hydrobromic acid is not readily decomposed by sulphuric acid; but on decomposing bromide of potassium by sulphuric acid, a little sulphurous acid is generally formed.

HYDROGEN and FLUORINE—HYDROFLUORIC ACID. ($h+f$) or hf or HF. This acid was made known by Scheele: the process for procuring it pure was first suggested by Mr. Knight (*Phil. Mag.*, xvii. 357.) Its properties were examined by Gay Lussac and Thenard in 1810. (*Recherches Physico-chimiques*.) When finely-powdered *fluoride of calcium*, or *fluor spar*, as it is usually called, (carefully selected for its purity,) is distilled with twice its weight of sulphuric acid, a highly volatile and corrosive liquid, which is *hydrofluoric acid*, is obtained; it acts powerfully on glass and most of the metals: the retort employed in the experiment may be of lead, with a tube and receiver of pure silver; the receiver must be immersed in a mixture of ice and salt. The product is best preserved in a silver bottle, with a well-fitted stopper of the same material. When pure, it is clear, colourless, very volatile, and smokes when exposed to air: at temperatures above 60° it flies off in vapour. Its specific gravity is 1.0609; but by the gradual addition of a certain proportion of water it acquires a considerable increase of density, the mixture having a specific gravity of 1.25. Its attraction for water exceeds that of sulphuric acid; and when dropped into water it excites a hissing noise, and great heat is evolved. Its vapour is dangerously pungent and irritating, and the liquid acid eminently active upon organic substances; a minute drop of it upon the skin produces a painful sore, and in larger quantities danger-

ous and malignant ulceration: hence the vessels containing it require to be handled with great caution. Its most characteristic property is the energy with which it acts upon glass: its vapours soon destroy the polish and transparency of all neighbouring glass vessels, and when dropped upon glass, great heat and effervescence are produced, and dense fumes evolved, consisting of *fluosilicic acid*. Diluted with about six parts of water, the acid may be used for *etching upon glass*, which it effectually accomplishes in a few minutes.

The nature of this powerful and peculiar acid is as yet imperfectly understood, its basis, *fluorine*, not having been obtained in an insulated form. All analogy, however, leads us to regard it as a compound of fluorine and hydrogen. In the voltaic circuit hydrogen is evolved from it at the negative electrode, and the positive platinum wire corroded and converted into a brown compound, probably of fluorine and platinum. Many of the metals also decompose it with the evolution of hydrogen; and peculiar compounds result, *fluorides*, consisting of the metal in combination with fluorine. The action of potassium upon this acid is very energetic; it is attended by explosion, by the liberation of hydrogen, and by the formation of a peculiar soluble saline compound, which is considered as a *fluoride of potassium*. Kuhlman's experiments are also quite consistent with these views: he found that pure fluor spar (fluoride of calcium) was not in the least acted upon, even at a red-heat, by anhydrous sulphuric acid; and that when hydrochloric acid was transmitted over fluor spar at a red heat hydrofluoric acid was disengaged and chloride of calcium formed. It cannot therefore be doubted that hydrofluoric acid, as originally suggested by Davy, is analogous to the other hydracids (*Phil. Trans.*, 1813, p. 263):

that it may therefore be regarded as composed of equal volumes of hydrogen and fluorine combined, without condensation. 100 cubic inches of its vapour would therefore weigh 20·2 grains, for,

Hydrogen.	Fluorine.		Hydrofluoric Acid.
1	18	=	19

50 cubic inches of hydrogen	. .	=	1·06
50 " " fluorine	. .	=	19·14
100			hydrofluoric acid = 20·20

Hence, therefore, its atomic constitution is

			Volumes.		Sp. Gr.
Hydrogen	. .	1 . . 1 . .	5·3 . .	1 . .	0·069
Fluorine	. .	1 . . 18 . .	94·7 . .	1 . .	1·288
Hydrofluoric acid	1	19	100·0	2	0·678

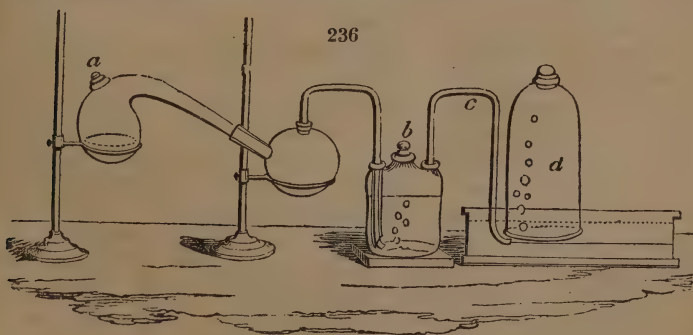
§ VII. NITROGEN.

NITROGEN, or *Azote* was first recognised as a distinct aëriform fluid by Dr. Rutherford in 1772. (Thesis, *De Aëre Mephitico*.) Dr. Priestley called it *phlogisticated air*.

Nitrogen may be obtained by burning phosphorus in a confined portion of atmospheric air. For this purpose a tall glass jar should be selected,

open at bottom, and stopped at the top: a small Wedgwood basin containing a sufficiency of inflamed phosphorus is then set afloat in the water-trough, and the jar, without its stopper, immediately inverted over it. A quantity of air is at first expelled by the heat: the stopper is then replaced, and the combustion goes on for some time; when it has ceased, and the apparatus has cooled, the basin is easily removed by agitating the jar, so as to sink it through the water; the residuary gas is then thoroughly washed with lime water, and is nitrogen nearly pure.

Another mode of obtaining nitrogen, which furnishes it in a state of considerably purity, consists in passing chlorine into a strong aqueous solution of ammonia. This may be done by nearly filling a Wolfe's bottle with two necks with the solution, and passing gaseous chlorine into it from a retort containing hydrochloric acid and oxide of manganese; a bent tube issuing from the other neck passes under the shelf of the pneumatic apparatus, and through it the nitrogen escapes, and may be collected; but care should be taken to leave excess of ammonia in the bottle. In this experiment ammonia, consisting of hydrogen and nitrogen (see AMMONIA), is decomposed by the chlorine, which unites with its hydrogen to form hydrochloric acid, and gaseous nitrogen is evolved: a solution of hydrochlorate of ammonia is at the same time obtained, and if excess of chlorine be used, chloride of nitrogen, a dangerously explosive compound, may be formed. If the ammoniacal solution be very concentrated, the bubbles of chlorine often produce flashes of light and slight explosions: these are harmless, and may be prevented by dilution of the ammonia. The following is the disposition of the apparatus: *a* is the retort and tubulated receiver containing the materials for the evolution of chlorine; *b* the two-necked bottle about three-fourths filled with strong liquid ammonia; *c* a bent tube, carrying the evolved nitrogen into the water-trough, where it is collected in the inverted jar *d*.



According to Berzelius, the purest nitrogen is obtained by filling a bottle about one-third full of a liquid amalgam of lead and mercury, carefully stopping it, and agitating it with the included air for two hours or more; the highly-divided lead absorbs the oxygen, and leaves pure nitrogen. On opening the bottle under water, the liquid rushes in, and demonstrates the degree of absorption.

If equal weights of iron-filings and sulphur be made into a paste with

water, and exposed to a confined portion of atmospheric air, it will, in the course of forty-eight hours, absorb the oxygen, and leave the nitrogen nearly pure.

There are many other processes by which nitrogen may be obtained, some of which will be further noticed under the article *Atmospheric Air*. It is also frequently evolved during the decomposition of animal matter. If lean muscular flesh, for instance, be heated in nitric acid diluted with ten or twelve parts of water, this gas is given off, though not pure: these cases of its evolution will be more particularly explained afterwards. When nitrogen gas is required deprived of moisture, it may be dried by exposure to fragments of quicklime, or of fused chloride of calcium.

Nitrogen is a permanently elastic colourless gas, with neither smell nor taste, having no action upon vegetable colours or upon lime-water; neither is it absorbed by water, except that fluid has been deprived of its ordinary portion of air by long boiling, when it takes up about one and a half *per cent.* Its refractive power in regard to light is to that of atmospheric air as 1.0340 to 1.0000. It is rather lighter than atmospheric air, compared with which its specific gravity is 0.972: 100 cubic inches weigh at mean temperature and pressure 30.16 grains. At 32° the weight of 100 cubic inches is 31.879 grains. (THOMSON.) Its specific gravity in reference to hydrogen is as 14 to 1.

An animal immersed in nitrogen is instantly suffocated, whence it was called by Lavoisier *azote* (from *a*, *privative*, and *ζωή*, life): but if that term be taken in its strict sense, all gaseous bodies (excepting atmospheric air) might be included under it; for even oxygen itself will not indefinitely support life: moreover, nitrogen, as it exists in the atmosphere, mixed with oxygen, appears to be absolutely essential to animal life; for no other gas can be substituted for it. Its influence in *respiration*, as a component of atmospheric air, will be considered afterwards. It is contained in almost every form of animal matter. If we consider the term *nitrogen* as merely implying that it is a component of nitric acid, it is explicit and unobjectionable; I, therefore, adopt it in preference to that of *azote*.

Nitrogen is, in the strictest sense of the word, a non-supporter of combustion; for all burning bodies are immediately and perfectly extinguished by it: this is the case with the flame of a taper, with phosphorus in intense combustion, and even with potassium, which, however highly heated, shows no inclination to burn in pure nitrogen.

The electro-chemical relations of nitrogen are still obscure, and whether it is or is not an ion has not been determined. How far it deserves to be called an *inflammable substance* is not obvious: its attraction for oxygen is not powerful, and the two bodies when mixed in their gaseous state show no tendency to combine; they do, however, unite in several proportions; but their compounds are formed at low temperatures; or the nitrogen and oxygen are presented to each other in their *nascent states*, that is, before one or both of them have acquired the independent gaseous form. The same remark applies to all compounds of this gas.

Under certain circumstances, however, nitrogen may be made to undergo a kind of combustion, as when electric sparks are passed through atmospheric air, or through a mixture of one volume of nitrogen with

two or three of oxygen; in this case each spark will be attended by the production of a trace of nitric acid, and after some hundred sparks, the blue of litmus will be changed to red (p. 325). Here combustion appears to take place in that portion of the gas immediately subject to the action of the sparks; but the temperature of the surrounding gas is not thus sufficiently elevated to enable the combustion to spread beyond the immediate sparks. Berzelius has well compared this action to that which ensues when sparks are passed through a mixture of hydrogen and a large relative quantity of atmospheric air or of oxygen; in that case no general combustion of the mixture is effected; but water is slowly formed by the action of each successive spark upon the portion of the gaseous mixture immediately subjected to its heating influence; and it is probable that the electric spark made to act upon mixtures of nitrogen and oxygen under considerable pressure might be more effective in inducing combination; but few of the nitric compounds are stable, or capable of sustaining a continued red heat without decomposition.

If a mixture of nitrogen with twelve or fourteen volumes of hydrogen be set fire to as it issues from a small tube, and burned either in common air or in an atmosphere of oxygen, water and nitric acid will be formed; so that in this case the nitrogen may be said to undergo combustion by the aid of the elevated temperature of the flame of hydrogen; but it must be recollected that in these cases nitric acid could not be produced without the presence of water, and that it may tend to dispose an union which would not otherwise take place. The formation of a trace of nitric acid when hydrogen is burned in common air is referable to the same cause.

Much discussion has arisen respecting the nature of nitrogen; and the question has been agitated, whether it is or is not a *simple body*; but although many ingenious surmises have been published on the subject, and many analogies suggested in favour of its compound nature, no experimental proofs have been hitherto adduced: Sir H. Davy (*Elements of Chem. Philos.*, 474) and Berzelius have each discussed this question, chiefly in reference to the phenomena of the supposed *metallisation of ammonia* (see MERCURY); and the latter has proposed the name *nitricum* for the imaginary base of nitrogen, assuming that gas to be a suboxide. (*Lehrbuch*, i. 208.) He has also adverted to the apparent formation of nitrogen by graminivorous animals, but this question will more properly be considered when upon animal products.

NITROGEN AND OXYGEN.—These bodies unite in *five proportions*, and form the compounds called,

1. Nitrous oxide	($n + 0$)
2. Nitric oxide	($n + 20$)
3. Hyponitrous acid	($n + 30$)
4. Nitrous acid	($n + 40$)
5. Nitric acid	($n + 50$)

PROTOXIDE OF NITROGEN. NITROUS OXIDE ($n + 0$) NO, or $\dot{\text{N}}$, was discovered by Dr. Priestley, in the year 1776; he called it *dephlogisticated nitrous air*: it has also been called *gaseous oxide of azote*. It may be formed by exposing *nitric oxide* ($n + 20$) to the action of iron-filings,

or of a mixture of sulphur and iron-filings, by which one equivalent of its oxygen is absorbed, and the remaining elements left in such proportions as to constitute nitrous oxide. But the gas thus procured is not pure. It is most easily and abundantly obtained in a state of purity by heating *nitrate of ammonia* in a glass retort over an Argand lamp, to a temperature of about 420° . The gas which passes off, provided the salt be pure, and the temperature not too high, may be collected over warm water, and is pure *nitrous oxide*. If the nitrate of ammonia contain a mixture of the hydrochlorate, the gas will be contaminated by chlorine; and if too much heat be used in the decomposition of the pure salt (which may be known by white vapours appearing in the retort) it will contain nitric oxide. The salt should be kept in a state of gentle ebullition, so as to maintain a quick but not violent evolution of gas.

The presence of *chlorine* in nitrous oxide is ascertained by its smell, and may be avoided by using pure nitrate of ammonia, the solution of which should not be rendered turbid by nitrate of silver. *Nitric oxide* is detected in it by the appearance of red fumes on mixing the gas with oxygen: it may be abstracted by agitating it with a solution of *protosulphate of iron*, which has no action upon nitrous oxide, but absorbs the nitric oxide, and acquires a deep olive colour. If nitrous oxide be mixed with *oxygen* or with *common air*, it affords red fumes upon adding to it a few bubbles of nitric oxide, and it is not, as it ought to be, entirely absorbed when agitated with thrice its bulk of cold water.

100 cubic inches of nitrous oxide weigh 47.220 grains; its specific gravity, therefore, to hydrogen, is as 22 to 1; and to atmospheric air as 1.524 to 1000. At the temperature of 32° , 100 cubic inches weigh 49.978 grains. (THOMSON.) Its taste is sweet, and its smell peculiar, but agreeable. It is absorbed when agitated with water, which takes up about its own bulk, and evolves it unchanged when heated; it should, therefore, be collected and preserved in stopped bottles.

Nitrous oxide was generally considered not only as unrespirable, but as eminently noxious; the attempts, however, that had been made to breathe it, were with an impure gas: when obtained perfectly pure, Sir H. Davy found that it might be breathed when mixed with common air, without any injurious effects, and he afterwards ventured upon its respiration in a pure state, and discovered its singular effects upon the system, which in many respects resemble those of intoxication. (*Researches Chemical and Philosophical, chiefly concerning Nitrous Oxide*. London, 1800.) The experiment of breathing this gas, however, cannot be made with impunity, especially by those who are liable to a determination of blood to the head. The following accounts will serve to give a general idea of its singular powers. They are quoted from Sir H. DAVY'S *Researches*, in which many important details concerning the effects of different gaseous bodies upon the system will be found. The first account is by Mr. Tobin, and the second by Dr. Roget:—

“On the 29th of April I breathed four quarts from and into a silk bag. The pleasant feelings produced at first, urged me to continue the inspiration with great eagerness. These feelings, however, went off towards the end of the experiment, and no other effects followed. The gas had probably been breathed too long, as it would not support flame.

I then proposed to Mr. Davy, to inhale the air by the mouth from one bag, and to expire it from the nose into another. This method was pursued with less than three quarts, but the effects were so powerful as to oblige me to take in a little common air occasionally. I soon found my nervous system agitated by the highest sensations of pleasure, which are difficult of description; my muscular powers were very much increased, and I went on breathing with great vehemence, not from a difficulty of inspiration, but from an eager avidity for more air. When the bags were exhausted and taken from me, I continued breathing with the same violence; then suddenly starting from the chair, and vociferating with pleasure, I made towards those that were present, as I wished they should participate in my feelings. I struck gently at Mr. Davy; and a stranger entering the room at the moment, I made towards him, and gave him several blows, but more in the spirit of good humour than of anger. I then ran through different rooms in the house, and at last returned to the laboratory somewhat more composed; my spirits continued much elevated for some hours after the experiment, and I felt no consequent depression either in the evening or the day following, but slept as soundly as usual."

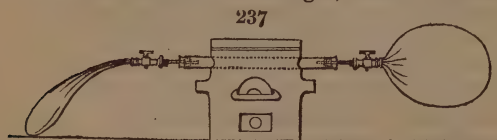
Dr. Roget states as follows:—"The effect of the first inspirations of the nitrous oxide was that of making me vertiginous, and producing a tingling sensation in my hands and feet; as these feelings increased, I seemed to lose the sense of my own weight, and imagined I was sinking into the ground. I then felt a drowsiness gradually steal upon me, and a disinclination to motion: even the actions of inspiring and expiring were not performed without effort; and it also required some attention of mind to keep my nostrils closed with my fingers. I was gradually roused from this torpor by a kind of delirium, which came on so rapidly that the air-bag dropt from my hands. This sensation increased for about a minute after I had ceased to breathe, to a much greater degree than before, and I suddenly lost sight of all the objects around me, they being apparently obscured by clouds, in which were many luminous points, similar to what is often experienced on rising suddenly and stretching out the arms, after sitting long in one position. I felt myself totally incapable of speaking, and for some time lost all consciousness of where I was, or who was near me. My whole frame felt as if violently agitated: I thought I panted violently; my heart seemed to palpitate, and every artery to throb with violence; I felt a singing in my ears; all the vital motions seemed to be irresistibly hurried on, as if their equilibrium had been destroyed, and everything was running headlong into confusion. My ideas succeeded one another with extreme rapidity, thoughts rushed like a torrent through my mind, as if their velocity had been suddenly accelerated by the bursting of a barrier which had before retained them in their natural and equable course. This state of extreme hurry, agitation, and tumult, was but transient. Every unnatural sensation gradually subsided; and in about a quarter of an hour after I had ceased to breathe the gas, I was nearly in the same state in which I had been at the commencement of the experiment. I cannot remember that I experienced the least pleasure from any of these sensations. I can, however, easily conceive, that by frequent repetition I might reconcile myself to them,

and possibly even receive pleasure from the same sensations which were then unpleasant. I am sensible that the account I have been able to give of my feelings is very imperfect. For, however calculated their violence and novelty were to leave a lasting impression on the memory, these circumstances were for that very reason unfavourable to accuracy of comparison with sensations already familiar. The nature of the sensations themselves, which bore greater resemblance to a half-delirious dream than to any distinct state of mind capable of being accurately remembered, contributes very much to increase the difficulty, and as it is above two months since I made the experiment, many of the minuter circumstances have probably escaped me."

Nitrous oxide is not permanently elastic; for by subjecting it to a pressure of about 50 atmospheres at the temperature of 45° , Mr. Faraday obtained it in the liquid form. It was thus procured by sealing up some nitrate of ammonia in a bent tube and heating it, while the other end was kept cool. Many explosions occurred with very strong tubes, and the experiment is always attended with risk. The tube, when cooled, is found to contain two fluids: the heavier is water, a little acid; the lighter, *liquid nitrous oxide*; it is limpid, colourless, and so volatile, that the heat of the hand generally makes it disappear in vapour. The application of ice and salt condenses it again. It has not been congealed by cold. Its refractive power is less than that of any known fluid. A tube being opened in the air, the nitrous oxide immediately burst into vapour. Another tube was opened under water, and the vapour collected and examined proved to be nitrous oxide. (*Phil. Trans.*, 1823, p. 195.)

Nitrous oxide supports combustion, and a taper introduced into it has its flame much augmented, and surrounded by a purplish halo. Phosphorus and sulphur, when introduced in a state of vivid ignition into this gas, are capable of decomposing it, and burn with the same appearance nearly as in oxygen; but if, when put into the gas, they are merely burning dimly, they then do not decompose it, and are extinguished; so that they may be melted in the gas, or even touched with a red-hot wire without inflaming. Charcoal, and many of the metals, also decompose nitrous oxide at high temperatures.

At a red heat this gas is decomposed, and two volumes of it are resolved into two volumes of nitrogen and one volume of oxygen, so that it thus suffers an increase of bulk. For experiments of this kind the following simple apparatus may be used; it consists of two bladders, one of which is filled with the gas, and the other empty, attached to the



extremities of a coated porcelain or platinum tube, which traverses the body of a furnace. The bladders are supplied with stop-cocks,

and the gas is squeezed from one to the other when the tube is red-hot.

The analysis of this gas may also be effected by detonation with hydrogen. When a mixture of one volume of nitrous oxide and one volume of hydrogen is fired by the electric spark, water is produced, and one volume of nitrogen remains. Now, as one volume of hydrogen takes

half a volume of oxygen to form water, nitrous oxide must consist of two volumes of nitrogen and one volume of oxygen; these three volumes being so condensed, in consequence of chemical union, as only to fill the space of two volumes. The specific gravity of nitrogen, compared with oxygen, is very nearly as 14 to 16; the composition, therefore, of the nitrous oxide, may be represented as annexed: and as

Nitrogen.	Oxygen.		Nitrous Oxide.
14	8	=	22

	Grains.
100 Cubic inches of nitrogen weigh	30·166
50 " oxygen 	17·054
100 " nitrous oxide 	47·220

Hence, regarding this gas as a *protoxide*, the equivalent number of nitrogen will be 14, or, according to Dr. Turner and Berzelius, 14·15 (*Phil. Trans.*, 1833), and nitrous oxide will be constituted as follows:—

				Davy.	Volumes.	S. G.	100 C.I.
Nitrogen	1	.. 14	.. 63·6	.. 63·3	.. 1·0	.. 0·97	.. 30·166
Oxygen	1	.. 8	.. 36·4	.. 36·7	.. 0·5	.. 0·55	.. 17·054
Nitrous oxide	1	22	100·0	100·0	1·0	1·52	47·220

DEUTOXIDE OF NITROGEN, BINOXIDE OF NITROGEN, NITRIC OXIDE, or NITROUS GAS, ($n + ^2O$) or \ddot{N} or NO^2 , was first procured by Mayow (*History of Chemistry*, p. 36), but its properties were first accurately studied by Priestley. It is usually obtained by presenting certain substances to *nitric acid*, which abstract a portion of its oxygen, leaving the remaining elements in such proportions as to constitute the gas in question; for this purpose some copper-filings or clippings may be put into a gas-bottle with nitric acid diluted with thrice its bulk of water; an action ensues, red fumes are produced, and there is a copious evolution of the gas, which may be collected and preserved over water. The first portions should be rejected, as containing nitrogen and nitrous acid gas. Nitric oxide is presently recognised by the red fumes which it produces when brought into the contact of air.

Nitric oxide is a colourless, uncondensable gas; its specific gravity to hydrogen is as 15 to 1. 100 cubic inches weigh 32·137 grains; and, compared with air, its specific gravity is as 1·038 to 1000. According to Thomson its specific gravity is 1·0416, and at the temperature of 32° 100 cubic inches weigh 34·1543 grains. Under common circumstances it is permanent over water; but if agitated with water previously deprived of air by long boiling, it is dissolved in the proportion of about 1 volume to 20. This solution, when long kept, is found to contain nitrate of ammonia, resulting from the joint decomposition of the nitric oxide and the water.

It is instantly fatal to animals; but as it will always meet with a sufficiency of oxygen in the lungs, to convert a part of it into nitrous acid, its abstract effects cannot be determined. An account of an attempt to breathe it will be found in Sir H. DAVY'S *Researches*, &c., p. 475. When it has been washed with water it is not acid, as may be proved by

the colour of litmus remaining unchanged by it. It extinguishes the flame of a taper, and that of sulphur, but phosphorus readily burns in it, if introduced in intense ignition, although it also is extinguished unless it be in vivid combustion. In this case the phosphorus decomposes the gas, nitrogen is evolved, and phosphoric acid formed. Charcoal also decomposes it at a high temperature, the results being carbonic acid and nitrogen.

Nitric oxide is not altered by a low red-heat, but it is decomposed when passed and repassed through small tubes heated to bright redness, more especially if the heated surface is increased by filling them with fragments of rock crystal: it does not detonate when mixed with two volumes of hydrogen, and subjected to the electric spark; a succession of sparks, however, passed through such a mixture, slowly effects the decomposition of a portion of the gas: the same mixture is also decomposed by spongy platinum at common temperatures, and water and ammonia are formed. When this mixture with hydrogen is kindled by a taper it burns with a green flame, and water and nitrogen are the products. Dr. Henry has shown that nitric oxide detonates with ammonia (*Phil. Trans.*, 1809,) in the proportion of 150 measures of the former to 100 of the latter. These gases also slowly act upon each other at common temperatures. Gay Lussac found that in about a month they were reduced to half their joint volume, and that nitrogen was evolved. Some substances which have a strong attraction for oxygen, effect a partial decomposition of the nitric oxide, and convert it, at common temperatures, into nitrous oxide; such, for instance, as moist iron-filings, some of the alkaline sulphurets, some of the sulphites, and protochloride of tin; in which cases two volumes of nitric oxide afford one of nitrous oxide. Nitric oxide may also be decomposed by the action of some of the metals at high temperatures, which absorb its oxygen. Sir H. Davy decomposed it by heated arsenic, and by the ignition of charcoal. (*Elements*, 260.) Gay Lussac

Nitrogen.	Oxygen.	Nitric Oxide.
14	8	
	8	30

decomposed 100 measures of it by the action of heated potassium: 50 measures of pure nitrogen remained, and the loss of weight corre-

sponded to 50 measures of oxygen; so that one volume of nitric oxide is thus resolved into equal volumes of oxygen and nitrogen. (*Mémoires d'Arcueil*.) Nitric oxide, therefore, is constituted of one volume of nitrogen and one volume of oxygen, combined as in the above diagram, without change of volume;

or 50 Cubic inches of nitrogen, weighing . . .	Grains.
and 50 " oxygen " . . .	15·083
form 100 " nitric oxide " . . .	17·054
	32·137

The following, therefore, is the composition of this gas:—

				Berzelius.	Vols.	Sp. Gr.	100 C.I.
Nitrogen . .	1 . .	14 . .	46·67 . .	46·754 . .	1 . .	0·97 . .	15·08
Oxygen . .	2 . .	16 . .	53·33 . .	53·246 . .	1 . .	1·11 . .	17·05
Nitric oxide	1 . .	30 . .	100·00 . .	100·000 . .	2 . .	1·04 . .	32·13

The most characteristic property of nitric oxide, by which it is immediately distinguished from all other gases, is, that of forming the red fumes of nitrous acid vapour when mixed with oxygen: hence these gases are mutually used to detect each other's presence; and as the nitrous acid is wholly absorbed by water, oxygen may be abstracted from any gaseous mixture containing it in an uncombined state, by the addition of a sufficient quantity of nitric oxide; and, on the other hand, nitric oxide may be removed by the addition of oxygen. Priestley, who was the first to attempt accurate experiments upon this subject, conceived that the absorption was at all times uniform; but subsequent experiments have shown that it is subject to variation, more especially dependent upon the presence or absence of water. Although, therefore, nitric oxide may be conveniently used to ascertain the presence of oxygen, it cannot be relied on as an indicator of its proportional quantity; and although Dalton (*Ann. of Phil.*, x. 38,) and Gay Lussac (*Mém. d'Arcueil*, ii. 247,) have each proposed methods by which they conceive accuracy may be ensured, they are not such as to admit of general application. The best mode of using the nitric oxide to determine the proportion of oxygen to that of nitrogen in the atmosphere, will be noticed under the head of Atmospheric Air (EUDIOMETERS).

Solutions of the protochloride and protosulphate of iron have the property of absorbing nitric oxide gas; the colour of these solutions is deep olive, and they speedily absorb oxygen when exposed to, or agitated with air, or other mixtures containing it. (See EUDIOMETERS.) This property also enables us to ascertain the purity of nitric oxide, which ought to be wholly absorbed by the solution of iron: some nitrogen or nitrous oxide are thus generally detected in it, and remain unabsorbed. According to Peligot (*Ann. C. and P.*, liv. 17), the proportion of nitric oxide absorbed by protosulphate of iron is definite, and in the ratio of one equivalent of the nitric oxide to four of the protoxide of iron; by exposure to a vacuum the nitric oxide escapes and the salt of iron remains unaltered; but when heated, a part only of the nitric oxide is evolved, and part is decomposed, and peroxide of iron and ammonia are formed: when this solution is exposed to air or oxygen, nitric acid is ultimately produced.

When nitric oxide is perfectly dry, chlorine exerts no action upon it, but the presence of water causes an immediate change; it is decomposed, and, furnishing oxygen to the nitric oxide, and hydrogen to the chlorine, nitrous and hydrochloric acids are generated. It was the presence of water which misled those who thought that the red fumes produced by mixing nitric oxide and chlorine, not carefully dried, resulted from the existence of oxygen in chlorine.

CHLORONITROUS GAS.—According to E. Davy (*Phil. Mag.*, ix. 355,) when fused chloride of sodium is moistened with nitric acid, a pale reddish yellow gas is evolved, composed of equal volumes of chlorine and nitric oxide, combined without condensation.

HYPONITROUS ACID. AZOTOUS ACID. NITROUS ACID of Graham, Berzelius, and most foreign authors. ($n + 30$) or \underline{n} , or NO_3 or $\ddot{\text{N}}$.—Gay Lussac concluded, from his experiments, that there exists a compound of nitrogen and oxygen intermediate between nitric oxide and nitrous acid,

which he termed *pernitrous acid*, but to which the term *hyponitrous acid* is more applicable. (*Ann. de Chim. et Phys.*, i. 399.) He found by mixing nitric oxide and oxygen in tubes standing over mercury, and containing a little concentrated solution of potassa, that 400 volumes of nitric oxide were condensed under such circumstances by 100 of oxygen. When, however, he attempted to decompose the *hyponitrite of potassa* thus obtained, nitric oxide was evolved, and nitrous acid formed. The liquid hyponitrous acid, he says, may be obtained by the distillation of nitrate of lead; it passes over in the form of a red vapour, condensable in a receiver surrounded by ice; it evolves nitric oxide when diluted with water: it boils at 80° . There is, however, reason to believe that the compound thus obtained is chiefly nitrous acid; but considerable difficulty occurs in reconciling the opinions of Gay Lussac and Berzelius upon these acids, the latter chemist applying the term *nitrous acid* (*Salpetrichte Säure*) to the pernitrous (hyponitrous) acid of the former.

Dulong obtained hyponitrous acid mixed with nitrous acid, by passing a mixture of 1 measure of oxygen with somewhat more than 4 of nitric oxide, first through a tube filled with fragments of porcelain to ensure perfect mixture, and afterwards through a bent tube, cooled below 0° : the acid collected in the curvature was a dark-green fluid, more volatile

Nitrogen.	Oxygen.
14	8
	8

than nitrous acid, and when distilled leaving a yellow fluid, which appeared to be nitrous acid. This acid, as well as the nitrous acid, appears to form a crystallizable compound with the hydrous sulphuric acid, which we shall describe afterwards. The component volumes of nitrogen and oxygen in the hyponitrous acid are, as in the

annexed diagram, 1 and 1.5; or it consists of

						Volumes.		
Nitrogen	..	1	..	14	..	36.8	..	} = Nitric oxide 2.0 Oxygen 0.5
Oxygen	..	3	..	24	..	63.2	..	
<hr/>								
Hyponitrous acid	1	..	38	..	100.0			

The hyponitrous acid appears to form distinct salts by combining with the salifiable bases. When, for instance, nitrate of potassa or nitrate of baryta are heated, oxygen is evolved, and a soluble *hyponitrite* remains. When nitric oxide gas is kept for some weeks in contact with a strong solution of potassa, it is partly converted into nitrous oxide, and the solution yields regular crystals of *hyponitrite of potassa*; 100 volumes of nitric oxide left 25 of nitrous oxide: the acid, therefore, which was absorbed, consisted of 100 volumes of nitrogen, and 150 of oxygen. According to Berzelius, several of the hyponitrites are best obtained by boiling metallic lead in a solution of nitrate of lead, by which a *hyponitrite of lead* is formed: this salt may then be decomposed by sulphates, which form sulphate of lead, and the hyponitrous acid unites to the base of the original sulphate.

When the acid liquid obtained by distilling nitrate of lead, is added to sulphuric acid, it forms a peculiar crystallizable compound. Nitric oxide is not of itself absorbed by sulphuric acid.

NITROUS ACID. HYPONITRIC ACID. PEROXIDE OF NITROGEN (Graham).

($n + 40$) or \bar{n} or NO_4 or $\ddot{\text{N}}$. When two volumes of nitric oxide and one volume of oxygen are mixed in an exhausted glass vessel, the gases combine with the evolution of heat consequent upon their mutual condensation, and form *nitrous acid vapour*, which is condensible into a liquid at 0° . The specific gravity of this liquid is 1.45; at 32° it is pale yellow; but at 60° deep orange: it boils at 82° , and when exposed to the air at common temperature, gradually evaporates in yellow fumes. (DULONG, *Ann. de Chim. et Phys.*, ii.) When a mixture of the gases, in the above proportions, is propelled through a tube cooled to 0° , the liquid acid is at once obtained, and it then appears the same as that obtained by the distillation of dry *nitrate of lead*. If the gases be mixed over water, hyponitrous acid and nitric acid are formed, and it is difficult in any way to obtain their total condensation or absorption by the water in the above proportions.

Nitrous acid vapour supports the combustion of phosphorus, and of charcoal, but extinguishes sulphur. It is readily absorbed by water. Its colour, like the liquid acid, varies with the temperature; becoming darker when heated, and paler when cooled; it has a very peculiar odour, which strongly adheres to the hair and to woollen clothing. Nitrous acid does not apparently unite with the bases, but forms with them *hyponitrites* and *nitrates*, hence it has been regarded as a compound of hyponitrous and nitric acids: when passed over baryta and other bases, at a temperature of between 300° and 400° , it is very rapidly absorbed with the evolution of heat, and the products are, according to Gay Lussac, as just stated. (*Ann. de Chim. et Phys.*, i.)

Nitrous acid vapour is constituted of one volume of nitrogen, and two

Nitrogen.	Oxygen.	
14	8	= Nitrous Acid. 46
	8	
	8	
	8	

will weigh 98.8 grains. It is, therefore, obviously constituted of

					Dulong.	Vols.	Sp. Gr.
Nitrogen	1	..	14	..	30.4	..	0.97
Oxygen	4	..	32	..	69.6	..	2.22
Nitrous acid	1	..	46	..	100.0	..	3.19

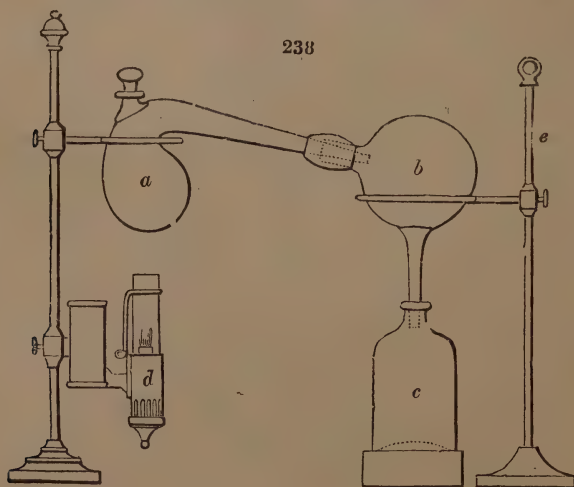
NITRIC ACID. AZOTIC ACID. ($n + 50$) or n' or NO_5 or $\ddot{\text{N}}$.—The composition of this acid was first demonstrated by Cavendish, in 1785, (*Phil. Trans.*) He produced it by passing a succession of electric sparks through a mixture of 7 volumes of oxygen and 3 of nitrogen. This experiment has more lately been verified by Faraday (p. 325.) Nitric acid is also formed when nitric oxide is slowly added to an excess of oxygen gas, over water. In this way 4 volumes of nitric oxide condense 3 volumes

of oxygen; but nitric oxide and oxygen never combine in these proportions without the presence of water, or a base.

Nitric acid is usually obtained by the distillation of purified *nitre* with sulphuric acid, of which materials different proportions are employed. The nitric acid of commerce, which is generally red and fuming, in consequence of the presence of nitrous acid, is procured by the distillation of two parts of nitre with one of sulphuric acid; these proportions afford about one part of orange-coloured nitric acid of the specific gravity of 1.48. Upon the large scale, 112 lbs. of nitre, and 56 of sulphuric acid, yield from 50 to 52 lbs. of nitric acid. Some manufacturers employ three parts of nitric and two of sulphuric acid, and the *London Pharmacopœia* directs equal weights, by which a nearly colourless nitric acid is afforded, provided the distillation be conducted at as low a temperature as possible. If the acid is not required in a concentrated state, the sulphuric acid may be previously diluted with its weight of water. Nitrate of soda being cheaper than nitrate of potassa, is also frequently resorted to as a source of nitric acid.

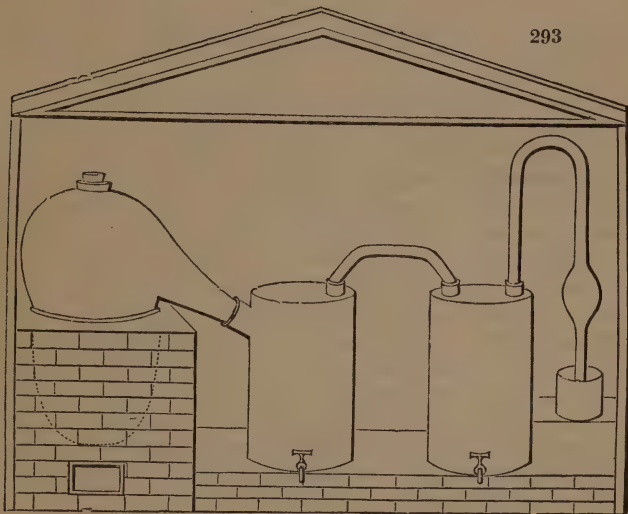
It will appear, by referring to the article *Sulphuric Acid*, that it contains in its liquid state one proportional of dry acid and *one* of water; whereas liquid nitric acid contains one proportional of dry acid and *two* of water: hence the requisite excess of sulphuric acid, where colourless and perfect nitric acid is to be obtained; hence, too, the red colour of the acid of commerce, in consequence of the smaller quantity of sulphuric acid generally used by the manufacturer, the deficiency of water occasioning the nitric acid to be resolved into nitrous acid and oxygen. This will be more apparent by reference to the article *Bi-sulphate of Potassa*. According to Mr. Phillips, the strongest nitric acid of commerce is a sesquihydrate, containing one atom of nitric acid and one and a half of water.

The distillation of nitric acid may be conducted upon the small scale in a tubulated glass retort *a*, with a tubulated receiver *b*, passing into the



bottle *c*. The requisite heat is obtained by the lamp *d*, and the whole apparatus supported by the brass stands with sliding rings *e e*.

But the manufacturer who prepares nitric acid upon a large scale, generally employs distillatory vessels of stone-ware. The following wood-cut represents the arrangement of the distillatory apparatus for the production of common *aqua fortis*: it consists of an iron pot, set in brick-work, over a fire-place; an earthen head is luted upon it, communicating with two or more receivers of the same material, furnished with earthenware stop-cocks, the last of which has a tube of safety dipping into a basin of water.



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The nitric acid of commerce, as obtained by the above processes, is always impure, and hydrochloric and sulphuric acids may generally be found in it. The former may be detected by *nitrate of silver*, and the latter by a dilute solution of *nitrate of baryta*. For pharmaceutical purposes, the ordinary acid is generally sufficiently pure. If, however, pure nitre and pure sulphuric acid be employed in its production, and the latter not in excess, there is little apprehension of impurity in the resulting acid. If the acid is coloured by the presence of nitrous acid, it is rendered colourless by boiling, which is best performed in a retort, with a loosely-attached receiver: the nitrous acid passes over.

Nitric acid is a colourless liquid, extremely sour and corrosive, and very intense in its action upon the greater number of inflammable bodies, to which it imparts oxygen, and by which it is resolved into some of the inferiorly-oxidized compounds. Its specific gravity, as usually obtained, fluctuates between 1.4 and 1.5. At 247° , when of the specific gravity 1.40, it boils and distils over without change, but the dilute acid is strengthened by boiling; and the strongest acid boils at a lower temperature than that which is of a somewhat less specific gravity. The following table of boiling-points has been given by Mr. Dalton, which shows that

the boiling-point of the acid of the specific gravity 1.42, composed of 1 atom of real acid and 4 atoms of water, is the maximum. This is called by Mr. Graham "the proper *nitrate of water*"; and of the four atoms of water which it contains, one is combined with the acid, as base, and may be named *basic water*, while the other three are in combination with the nitrate of water, and may be termed the *constitutional water* of the salt." He represents this acid in symbols, thus, $\text{HO}, \text{NO}_5 + 3\text{HO}$.

Acid of specific gravity 1.50 boils at 210°

"	1.45	"	240
"	1.42	"	248
"	1.40	"	247
"	1.35	"	242
"	1.30	"	236
"	1.20	"	226
"	1.15	"	219

At -40° the concentrated acid congeals. When diluted with half its weight of water it freezes at about -2° . When exposed to the air it exhales fumes, and gradually absorbs water, so that its bulk becomes increased, and its specific gravity diminished. It suffers a partial decomposition when exposed to light, becoming yellow and evolving oxygen, so that it should be kept in a dark place, and especially excluded from the direct rays of the sun. By distilling nitric acid (sp. gr. 1.4) twice successively from four times its weight of sulphuric acid, Gay Lussac increased its density to 1.510. In this state he found it remarkably susceptible of decomposition by heat or light. (*Ann. de Chim. et Phys.*, i.) According to Thenard, a mixture of 1 part of nitric and 4 of sulphuric acid gently heated, affords oxygen and nitrous acid, the sulphuric acid becoming diluted by the abstraction of the water of the nitric acid.

When nitric acid is mixed with snow, the latter is suddenly liquified, and intense cold is produced. Nitric acid, of the sp. gr. 1.5, mixed with half its bulk of water, occasions an elevation of temperature in the mixture $= 112^\circ$: 58 parts of the acid with 42 of water, both at 60° , give, on mixture, a temperature of 140° . (URE, *Quarterly Journal*, iv. 298.) On diluting the red fuming acid it assumes various tints of blueish green dependent upon the quantity of water added.

Nitrogen.	Oxygen.
14	8
	8
	8
	8
	8

Nitric acid has not been obtained in a *dry*, or anhydrous state; the liquid acid is a compound of the anhydrous acid and water, or in the language of Mr. Graham, a *nitrate of water*, and some of the salts called *nitrates*, (such as *nitrate of potassa*), are compounds of the anhydrous acid, and a salifiable base. The *anhydrous nitric acid* is constituted of one volume of nitrogen and two volumes and a half of oxygen, as in the annexed diagram.

It is therefore a compound of

					Lavoisier.	Cavendish.	Berzelius.	
Nitrogen	. 1	..	14	..	25.9	.. 20	.. 25	.. 26
Oxygen	. 5	..	40	..	74.1	.. 80	.. 75	.. 74
	1		54		100.0	100	100	100

The liquid nitric acid in its utmost state of concentration (sp. gr. 1·5), consists, according to Phillips, of one equivalent of anhydrous acid and one and a half of water. According to Dr. Ure, the acid of a specific gravity of 1·486 contains one equivalent of real acid and two of water: hence the following table:—

	Sp. gr.=1·5.			Sp. gr.=1·486.		
Anhydrous acid	1	54	80	1	54	75
Water	1½	13·5	10	2	18	25
	1	67·5	100	1	72	100

The following table, drawn up by Dr. Ure, exhibits the quantity of dry acid and of liquid acid (sp. gr. 1·5) at different densities; (*Quarterly Journal*, iv. 297, and *Dictionary*, p. 71, Sec. Edit;) the quantity of anhydrous acid in the liquid acid of sp. gr. 1·50 being assumed = 79·7. The column of dry acid shows the weight which any salifiable base would gain by uniting with 100 parts of the liquid acid of the corresponding specific gravity.

Specific gravity.	Liquid acid in 100.	Dry acid in 100.	Specific gravity.	Liquid acid in 100.	Dry acid in 100.	Specific gravity.	Liquid acid in 100.	Dry acid in 100.
1·5000	100	79·700	1·3783	66	52·602	1·1895	33	26·301
1·4980	99	78·903	1·3732	65	51·805	1·1833	32	25·504
1·4960	98	78·106	1·3681	64	51·068	1·1770	31	24·707
1·4940	97	77·309	1·3630	63	50·211	1·1709	30	23·900
1·4910	96	76·512	1·3579	62	49·414	1·1648	29	23·113
1·4880	95	75·715	1·3529	61	48·617	1·1587	28	22·316
1·4850	94	74·918	1·3477	60	47·820	1·1426	27	21·519
1·4820	93	74·121	1·3427	59	47·023	1·1465	26	20·722
1·4790	92	73·324	1·3376	58	46·226	1·1403	25	19·925
1·4760	91	72·527	1·3323	57	45·429	1·1345	24	19·128
1·4730	90	71·730	1·3270	56	44·632	1·1286	23	18·331
1·4700	89	70·933	1·3216	55	43·835	1·1227	22	17·534
1·4670	88	70·136	1·3163	54	43·038	1·1168	21	16·737
1·4640	87	69·339	1·3110	53	42·241	1·1109	20	15·940
1·4600	86	68·542	1·3056	52	41·444	1·1051	19	15·143
1·4570	85	67·745	1·3001	51	40·647	1·0993	18	14·346
1·4530	84	66·948	1·2947	50	39·850	1·0935	17	13·549
1·4500	83	66·155	1·2887	49	39·053	1·0878	16	12·752
1·4460	82	65·354	1·2826	48	38·256	1·0821	15	11·955
1·4424	81	64·557	1·2765	47	37·459	1·0764	14	11·158
1·4385	80	63·760	1·2705	46	36·662	1·0708	13	10·361
1·4346	79	62·963	1·2644	45	35·865	1·0651	12	9·564
1·4306	78	62·166	1·2583	44	35·068	1·0595	11	8·767
1·4269	77	61·369	1·2523	43	34·271	1·0540	10	7·970
1·4228	76	60·572	1·2462	42	33·474	1·0485	9	7·173
1·4189	75	59·775	1·2402	41	32·677	1·0430	8	6·376
1·4147	74	58·978	1·2341	40	31·880	1·0375	7	5·579
1·4107	73	58·181	1·2277	39	31·083	1·0320	6	4·782
1·4065	72	57·384	1·2212	38	30·286	1·0267	5	3·985
1·4023	71	56·587	1·2148	37	29·489	1·0212	4	3·188
1·3978	70	55·790	1·2084	36	28·692	1·0159	3	2·391
1·3945	69	54·993	1·2019	35	27·895	1·0106	2	1·594
1·3882	68	54·196	1·1958	34	27·098	1·0053	1	0·797
1·3833	67	53·399						

Dr. Thomson has constructed the following table showing the specific gravity of various atomic combinations of nitric acid and water. (*First Principles*, i. 114.)

Atoms of Acid.	Atoms of Water.	Acid in 100 parts.	Specific Gravity.
1	1	85·714	1·5500
1	2	75·009	1·4855
1	3	66·668	1·4546
1	4	60·000	1·4237
1	5	54·545	1·3928
1	6	50·000	1·3692
1	7	46·260	1·3456
1	8	42·857	1·3220
1	9	40·000	1·3032
1	10	37·500	1·2844
1	11	35·294	1·2656
1	12	32·574	1·2495
1	13	31·579	1·2334
1	14	30·000	1·2173
1	15	28·571	1·2012

Nitric acid may be decomposed by passing its vapour through a red-hot porcelain tube; oxygen is given off, nitrous acid gas is produced, and a quantity of diluted acid passes over into the receiver, having escaped decomposition; so that it is thus proved to consist of nitrous acid, oxygen, and water. At a white heat, oxygen, nitrogen, and water, only, are evolved. When strong nitric acid was electrolysed, no gas appeared at the negative electrode, but nitrous acid, and apparently nitric oxide, were formed there, which rendered the acid red and effervescent. In dilute nitric acid, gas appeared at the negative electrode, its quantity being varied by variations either in the strength of the acid or of the voltaic current: the gas at the anode was always oxygen, that at the cathode, hydrogen. When the quantity of products was examined by the voltameter, the oxygen, whether from strong or weak acid, was always in the same proportion as from water. When the acid was diluted to sp. gr. 1·24 or less, the hydrogen also proved to be in the same quantity as from water; hence Mr. Faraday concludes, that nitric acid does not undergo electro-chemical decomposition, but the water only: that the oxygen at the anode is always a primary result, but that the products at the cathode are often secondary, and due to the reaction of the hydrogen upon the acid. (*Phil. Trans.*, 1834, 96.)

According to Mr. Daniell the result of the electrolysis of nitric acid, composed of one atom of anhydrous acid and one of water, is attended by the evolution of hydrogen at the cathode, and of a compound (which he calls *oxynitron*) of 1 atom of nitrogen and 6 of oxygen, at the anode; hence $(n + 5o) + (h + o)$ becomes in such case $(n + 6o) + h$. (*Phil. Trans.*, 1840, p. 223.)

When nitric oxide is passed through concentrated nitric acid, it is decomposed, and nitrous acid is formed, partly by the acquisition of oxygen by the oxide, and partly by its loss by the acid. Dr. Turner observes, that "The nitrous acid thus derived from two sources gives a colour to the nitric acid, the depth and kind of which depend upon the quantity of the deutoxide of nitrogen which has been employed. The

first portion communicates a pale straw-colour, which gradually deepens as the absorption of the deutoxide continues, till the nitric acid has acquired a deep orange hue, together with all the characters of strong, fuming nitrous acid. But the solution still continues to absorb the deutoxide, and, in doing so, its colour passes through different shades of olive and green, till it becomes greenish-blue. By applying heat to the blue liquid, the deutoxide of nitrogen is evolved, and in proportion as it escapes, the colour of the solution changes to green, olive, orange, and yellow; at length becoming pale as at first. Nitrous acid vapours are likewise disengaged as well as the deutoxide. These phenomena are very favourable to the view that the conversion of the orange-colour into olive, green, and blue, is owing to the formation of hyponitrous acid." (*Elements of Chem.*, 5th ed., 290.)

Some of the metals, such as copper, tin, and silver, are at first without action on concentrated nitric acid, but become vehemently active upon the addition of a little water. It often happens, in such cases, that the metal combines with the oxygen of the water, and that the evolved hydrogen unites to the nitrogen of the acid, forming ammonia, which combines with the undecomposed acid. Poured upon hot iron-filings or melted bismuth, zinc, or tin, nitric acid causes a combustion of the metals.

The facility with which nitric acid imparts oxygen, renders it a valuable oxidizing agent in many chemical operations: phosphorus and most of the metals decompose it at common temperatures, and sulphur and carbon, when aided by heat. It acts energetically often, when diluted, upon the greater number of animal and vegetable substances, and mutual decompositions ensue. A drachm of oil of turpentine mixed with half a drachm of sulphuric acid, instantly bursts into flame upon the addition of a drachm of nitric acid. A piece of glowing charcoal thrown upon the surface of the concentrated acid, burns vehemently with the evolution of red fumes (BERZELIUS). Oxalic, malic, and carbonic acids, are the common products of the action of dilute nitric acid upon most vegetable and animal substances: fatty matter, ammonia, and hydrocyanic acid are also sometimes formed. It tinges the greater number of animal substances of a yellow colour, and permanently stains the nails and cuticle; it is hence employed in the production of yellow patterns upon coloured woollen goods. It is used in fumigations to destroy contagious and infectious matter, more especially in inhabited apartments, where chlorine would prove injurious; for this purpose nitrate of potassa and sulphuric acid are mixed in a saucer, and the evolution of the nitric acid vapour aided by a gentle heat; but it is not so effective as chlorine. In pharmacy, and a variety of other processes, it is susceptible of interesting applications: it is used for etching on copper, and as a solvent for tin in the preparation of valuable mordants used by dyers and calico printers: it is an important agent in metallurgy, and especially in the art of assaying. In medicine it is prescribed as a tonic; and occasionally in syphilitic, hepatic, and eruptive disorders; and in surgery as an energetic caustic. In the bite of rabid animals, if immediately applied to the wound, there is every reason to believe that it would destroy the poison and prevent its consequences.

The salts which nitric acid forms, and which are termed *nitrates*, are all soluble in water; and hence neither its presence nor quantity can be determined by any precipitating re-agent. When uncombined, it is easily recognised by the facility with which it attacks copper, causing the evolution of nitric oxide, and affording a blue solution; and by the formation of *nitre*, when it is saturated with potassa, which salt readily crystallizes in long six-sided prisms. When hydrochloric acid is added to a solution of a *nitrate*, chlorine is evolved, and the liquid acquires the power of dissolving gold-leaf; but as the action of hydrochloric acid on the salts of chloric and bromic acid also furnishes a solution which dissolves gold, no inference can be drawn from the experiment, except the absence of those acids has been previously ascertained.

The following method of detecting the presence of nitric acid has been suggested by Dr. Liebig, who says that it is effective when not more than a four-hundredth part of the acid is present. The liquid to be examined must be mixed with a sufficiency of sulphuric solution of indigo, to acquire a distinct blue colour; a few drops of concentrated sulphuric acid are then added, and the whole boiled; if the liquid contain a nitrate, it will either be bleached or rendered yellow. By adding a little common salt to the liquid before applying heat, a five-hundredth part of nitric acid may easily be discovered. (*Ann. de Chim. et Phys.*, xxxv. 80.)

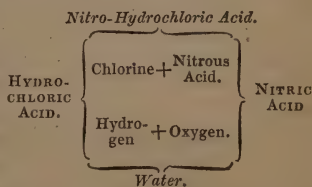
M. Runge proposes to detect nitric acid and its combinations as follows:—"Pour a solution of proto-chloride of iron upon the surface of an amalgam of zinc, and then place a crystal of nitre on the latter in the fluid: a dark band immediately forms around the crystal, sometimes extending over the whole surface of the amalgam. All the nitrates, as well as nitric acid, act in this manner; but other salts, such, for instance, as the chlorates, produce no such effect, so that a very sensible test of the presence of nitric acid is thus afforded. It is necessary that the solution employed be a proto-salt of iron. If nitric acid is supposed to exist in a liquid, it should be saturated with potassa, evaporated to dryness, and the dry mass tried. Salts of copper and silver must not be present." (*Annalen der Physik*, 1827.)

Another test for nitric acid has been proposed by Richemont: the liquid suspected to contain a nitrate is mixed with an equal bulk of sulphuric acid, and when cool a few drops of a strong solution of protosulphate of iron are added; nitric oxide is evolved, which produces a purplish tint, even when the quantity of nitric acid is very small. Dr. Turner observes that another character which may be useful consists in mixing the supposed nitric acid or nitrate with dilute sulphuric acid, in a tube, adding a few fragments of zinc, and setting fire to the hydrogen as it issues; if nitric acid be present the flame of the hydrogen will have a greenish-white tint, due to the admixture with binoxide of nitrogen. "A very delicate test," he adds, "has been proposed by O'Shaugnessy, founded on the orange red, followed by a yellow colour, which nitric acid communicates to morphia. The supposed nitrate is heated in a test tube with a drop of sulphuric acid, and then a crystal of morphia is added. It is advisable to try the process in a separate tube with the sulphuric acid alone, in order to prove the absence of nitric acid in it."

Nitric acid is an important agent in the operations of analysis. It is

used,—1. to oxidize and dissolve the metals, and to separate them from the few which are not acted upon by it, especially gold and platinum: it is of constant use in the process of assaying, for separating silver from gold. 2. To separate certain metals in the form of insoluble peroxides, such as antimony and tin, from those which yield soluble oxides, as in the separation of tin from mercury; it also is useful in the peroxidization of iron and manganese, by which those metals are rendered insoluble in nitric acid, and thus separable from soluble earths, &c. 3. Dilute nitric acid separates sulphur from the metals in the form of an insoluble magma, or gray powder, as in the analysis of sulphuret of copper, of lead, or of silver; if concentrated, it acidifies sulphur and arsenic. 4. The concentrated acid detects sulphuretted hydrogen by the production of a white cloud, and the destruction of its fetid odour. 5. It is used as a solvent to determine the nature of certain precipitates, and to separate the soluble from the insoluble. The precipitates formed by the vegetable acids, by succinic acid, by phosphoric acid, and by arsenic acid in the solutions of baryta, of lime, and of lead, are easily soluble in dilute nitric acid; but the precipitate by sulphuric acid in solutions of baryta is perfectly insoluble, and that in solution of lead difficultly soluble, requiring about 100 parts of the acid. 6. Nitric acid is a test of certain organic substances: it generally tinges those containing nitrogen of a yellow colour; it detects strychnia, by rendering it red; the nitric solution of uric acid leaves a red residue on evaporation; it changes polychroite to green, and guaiacum to blue and green. It distinguishes gum from starch, by converting the former into mucous or sacclactic acid: cork it converts into suberic acid. 7. Many of the nitrates, and the nitro-hydrochloric acid, are used as tests. (PFAFF, *Handbuch der Analytischen Chemie*, i. 98, 2nd ed.)

NITRO-HYDROCHLORIC ACID. NITRO-MURIATIC ACID.—This term has been applied to the *Aqua Regia* of the alchemists. When nitric and hydrochloric acids are mixed, they become yellow, and acquire the power of dissolving gold, which neither of the acids possessed separately. This mixture evolves chlorine, a partial decomposition of both acids having taken place, and water, chlorine, and nitrous acid are thus produced; that is, the hydrogen of the hydrochloric acid abstracts oxygen from the nitric to form water: the result must be chlorine and nitrous acid. (DAVY, *Journal of Science and the Arts*, vol. i., p. 67.) The annexed diagram may, perhaps, serve to render these mutual changes more evident. Two parts of hydrochloric and one of nitric acid furnish the most effective mixture; but a solution having the same general properties is obtained by adding nitre to hydrochloric acid, or common salt to nitric acid. According to Berzelius, the mutual decomposition of the two acids proceeds only so far in the first instance as to saturate the liquid with chlorine; but when heat is applied, chlorine is evolved till one of the acids is entirely decomposed. When a metal is put into nitro-hydrochloric acid, it absorbs the chlorine,



and is dissolved; for the liquid cannot become then saturated with chlorine, because the metal combines with it as fast as it is evolved: the application of heat greatly accelerates this action, but much chlorine may be lost by employing too high a temperature. As nitric oxide is evolved during the solution of a metal in nitro-hydrochloric acid, it might be supposed that the hydrogen of the hydrochloric acid had reduced the nitric acid to the state of nitric oxide; but Davy has shown that a mixture of hydrochloric and *nitrous* acids possesses none of the properties of Aqua Regia: consequently, the evolution of nitric oxide depends upon the spontaneous resolution of the produced nitrous acid into nitric acid and nitric oxide. Nitro-hydrochloric acid is the common solvent of gold and platinum, and may, with proper precautions, be used in the separation of those metals from silver, which remains as an insoluble chloride. It furnishes a useful solution of tin; and is employed in the analysis of minerals containing sulphur, to separate and acidify that elementary body.

NITROGEN AND CHLORINE. CHLORIDE OF NITROGEN. TERCHLORIDE OF NITROGEN. ($n + 3C$) or $N Cl_3$.—These gases do not unite *directly*, but the compound may be obtained by exposing a solution of *nitrate* or *hydrochlorate of ammonia* to the action of chlorine, at a temperature of 60° or 70° . The gas is absorbed, and an oil-like fluid, heavier than water, is produced by the union of the nascent nitrogen (evolved in the decomposition of the ammonia of the salt) with the chlorine. It was discovered by M. Dulong, in 1812, (*Ann. de Chim.*, LXXXV.,) and its properties afterwards investigated by Davy. (*Phil. Trans.*, 1813.)

The simplest mode of obtaining this compound, consists in filling a perfectly clean glass basin with a solution of about one part of sal-ammoniac in twelve of water, and inverting into it a tall jar of chlorine. The saline solution is gradually absorbed, and rises into the jar, a film forms upon its surface, and it acquires a deep yellow colour: at length small globules, looking like yellow oil, collect upon its surface, and

240



successively fall into the basin beneath, whence they are most conveniently removed by drawing them into a small and perfectly clean glass syringe, made of a glass tube drawn to a pointed orifice (fig. 240), and having a copper-wire with a piece of clean tow wrapped round it for a piston; in this way a globule may be drawn into the tube, and transferred to any other vessel. Balard obtained this compound by suspending a piece of sulphate of ammonia in a strong solution of hypochlorous acid.

The specific gravity of chloride of nitrogen is 1.6; it is not congealed by cold. Its odour is irritating and peculiar; it very soon evaporates when exposed to air. It is dangerously explosive, and is decomposed with violent detonation by many combustibles, especially phosphorus and fixed oils. In making these experiments, which should be conducted with extreme caution, and the face protected by a mask (Dulong lost an eye and the use of a finger, and Sir H. Davy was wounded in the face

by the effects of its detonation), a small globule of the compound, about the size of a mustard seed, may be cautiously transferred to a clean porcelain basin, half filled with water, and placed under a wire-cage: a very small piece of phosphorus, fixed to the end of a long stick, or a long rod with the extremity dipped in oil, may be then brought into contact with the globule, which instantly explodes with a flash of light, dispersing the water, and breaking the basin to atoms. At 160° it distils without change, but at 212° it explodes, and is decomposed. It was submitted to the action of 125 different substances, by Messrs. Porret, Wilson, and Kirk, of which the following caused it to explode.

* Phosphorus	Linseed-oil	Oil of orange-peel
Phosphuret of lime	Olive-oil	Naphtha
Caoutchouc	Camphorated oil	Strong liquid ammonia
Myrrh	Sulphuretted oil	Fused potassa
Palm-oil	Oil of turpentine	Phosphuretted hydrogen
Ambergris	Oil of tar	Nitric oxide
Whale-oil	Oil of amber	Metallic soaps.

The metals, resins, and sugar, did not cause it to explode. (NICHOLSON'S *Journal*, vol. xxxiv.) Alcohol quietly changes it into a white substance. Mercury and most of the other metals absorb the chlorine, and evolve nitrogen. It gradually disappears when kept in a stopped phial with water, and nitrous and hydrochloric acid are formed by the mutual decomposition of the liquids. In concentrated hydrochloric acid it forms ammonia, and chlorine is evolved. It is also slowly decomposed by dilute liquid ammonia; hydrochlorate of ammonia is formed, and nitrogen evolved.

The existence of nitrogen in nearly all the powerfully-detonating bodies is a singular fact, and the decomposition of this compound is attended by a circumstance observed in some other cases, namely, the appearance of flame or fire, which is here, not the result of condensation and union, but is accompanied by expansion and decomposition; by the separation of two bodies previously combined: the decomposition of the oxides of chlorine already referred to, and that of iodide of nitrogen and of peroxide of hydrogen (oxygenated water) exhibits the same peculiarity.

Chloride of nitrogen appears to yield, by decomposition, 1 volume of nitrogen and 3 of chlorine (and not 4, as originally inferred by Davy); and as the specific gravity of nitrogen to chlorine is as 14 to 36, so it may be said to consist of 1 volume of nitrogen + 3 volumes of chlorine, and, in the state of vapour, it is probable that the four volumes of æriform matter which it affords by decomposition, are condensed into one. It is, therefore, regarded as a compound of

Nitrogen.	Chlorine.	
14	36	
	36	=
	36	36

Nitrogen	1	14	11.5
Chlorine	3	108	88.5
<hr/>			
Chloride of Nitrogen	1	122	100.0

From the experiments of Millon it seems probable that this compound may contain hydrogen. (*Ann. de Ch. et Ph.*, Lxix. 75.)

NITROGEN AND IODINE. IODIDE OF NITROGEN. TERIODIDE OF NITROGEN. ($n + 3i$) or NI_3 .—This compound may be procured by pouring a solution of ammonia upon a very small quantity of iodine. The iodine decomposes part of the ammonia, and, combining with its hydrogen, forms hydriodic acid, and this, uniting with the ammonia, forms hydriodate of ammonia: the nascent nitrogen unites with another portion of iodine, and forms an insoluble black powder, which may be collected by pouring off the liquid, and placing it, while moist, in small parcels upon bibulous paper, where it must be suffered to dry spontaneously. This curious compound was discovered by Courtois. Serullas obtains it by agitating alcoholic solution of iodine with excess of ammonia; it subsides on dilution with water, and must be carefully dried: in this state it does not detonate whilst moist, but if it is put into pure ammonia it explodes when slightly pressed in the liquid. (*Ann. de Chim. et Phys.*, xlii. 201.) Mitscherlich (POGGENDORFF'S *Annalen.*, xiv. 539) has described another method of obtaining this compound. A chloride of iodine is formed by dissolving iodine in nitro-hydrochloric acid; this solution, saturated with ammonia, yields hydrochlorate of ammonia and iodide of nitrogen: the latter may be collected upon a filter, and separated, whilst moist, into small portions; but it is not safe to operate upon more than a few grains of iodine. In this experiment no gas is evolved; one proportional of ammonia reacts upon three proportionals of chloride of iodine, so that a volume of nitrogen combines with three volumes of iodine vapour to produce the detonating compound, and three volumes of hydrogen combine with three of chlorine to form hydrochloric acid.

Iodide of nitrogen, when dry, detonates upon the slightest touch, and the detonation of one portion generally causes the neighbouring ones to explode also. When it detonates, the purple fumes of iodine are perceptible. When left exposed to air it slowly evaporates; and if moist, is gradually resolved into nitrogen or ammonia, and iodic and hydriodic acids. It is decomposed by hot water and by alkaline solutions. Marchand has attempted to show that this compound contains hydrogen (*Ann. de Ch. et Ph.*, Lxxiii. 222), but from Gay Lussac and Colin's researches (*Ann. de Ch.*, xci. 30), it appears to consist of

Nitrogen . . .	1 . .	14 . .	3.6
Iodine . . .	3 . .	375 . .	96.4
<hr/>		<hr/>	<hr/>
Iodide of nitrogen	1	389	100.0

BROMIDE OF NITROGEN ($n + 3b$), or NBr_3 , is obtained, according to M. Millon, (*Ann. de Ch. et Ph.*, Lxix. 75,) by gradually adding a solution of an alkaline bromide to the chloride of nitrogen under a thin stratum of water: with bromide of potassium, for instance, bromide of nitrogen and chloride of potassium are the results. Bromide of nitrogen is of dark red colour, and more readily decomposed than the chloride; it has an oily aspect, is heavy, very volatile, and its vapour fetid and very irritating to the eyes. Phosphorus and arsenic cause it to detonate with great

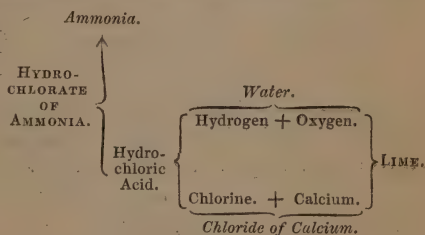
violence: its general characters are analogous to those of the chloride. According to Millon it contains hydrogen, but its composition is probably the counterpart of the chlorides of nitrogen and iodine.

NITROGEN AND HYDROGEN. AMMONIA. VOLATILE ALKALI. TERHYDRURET OF NITROGEN. ($n + 3h$) or A, or NH_3 . — When nitrogen and hydrogen gases are mixed, they show no tendency to combine; they unite, however, under certain peculiar circumstances of evolution, and the result is *ammonia*. This gaseous compound may be obtained by heating a mixture of *quicklime* and *hydrochlorate of ammonia*. Two parts of dry quicklime and one of hydrochlorate of ammonia may be introduced into a small glass retort, and, upon the application of a gentle heat, the gas is evolved. It must be collected over mercury. Towards the latter part of the operation water passes over, which may be arrested in the neck of the retort by the previous introduction of a piece of blotting-paper; or it may be prevented passing over by filling up the bulb of the retort with powdered lime. The theory of the decomposition which here ensues is somewhat complicated, and will be better understood when the nature of lime is explained. Hydrochlorate of ammonia is a compound of hydrochloric acid and ammonia; by the action of the lime (which is an oxide of calcium) the ammonia is expelled in its pure and gaseous form: the hydrochloric acid and the lime then mutually decompose each other, and water and chloride of calcium are the results. The annexed diagram may, perhaps, more clearly explain this.

Ammonia is permanently elastic at common temperatures; by exposing it to intense cold, Guyton supposed that he had observed it to assume a liquid form. (*Ann. de Chim.*, xxix. 290.) But this could not be the case, as it requires for its liquification a pressure of 6·5 atmospheres at the temperature of 50°. (*FARADAY, Phil. Trans.*, 1823, p. 196.) It was most readily obtained in this state by disengaging it in a sealed tube from chloride of silver, which had been previously made to absorb it. It was colourless, transparent, of a specific gravity of 0·76, and its refractive power surpassed that of water.

Ammonia is very pungent and acrid, and of course unrespirable, but when diluted by mixture with common air, agreeably stimulant. It converts most vegetable blues to green, and the yellows to red, properties which belong to the bodies called *alkalis*. Ammonia, therefore, has been termed *volatile alkali*; and the change of colour thus effected by it, is distinguished from that produced by the *fixed* alkalis, by the return of the original tint, when the ammonia flies off by exposure. It saturates the acids, and produces an important class of *ammoniacal salts*, which are recognised by the evolution of ammonia when they are triturated with potassa, soda, or lime.

The specific gravity of ammonia compared with hydrogen is as 8·5 to



1; compared with air it is as 0.590 to 1; 100 cubical inches weigh 18.28 grains; or, at the temperature of 32° , 19.301 grains. (THOMSON.) It extinguishes flame, but forms a difficultly inflammable mixture with common air, and may be burned when issuing from a capillary orifice in an atmosphere of oxygen. When mixed with its volume of oxygen it burns with a feeble explosion. Ammonia is abundantly absorbed by chloride of calcium, as well as by several other chlorides, with which, and with the other haloids, it forms a curious and interesting series of compounds which will afterwards be noticed. If it be required artificially to dry the gas, potassa or lime should be used. (*Quarterly Journal*, v. 74.)

Water, at the temperature of 50° , takes up 670 times its volume of ammonia (780, THOMSON); its bulk is increased, and its specific gravity diminished; that of a saturated solution is 0.875, water being 1.000. The following table shows the quantity of ammonia in solutions of different specific gravities. (DAVY'S *Chem. Phil.*, p. 268.)

100 parts of Sp. Gr.		Of Ammonia.	100 parts of Sp. Gr.		Of Ammonia.
8750	contain	32.50	9435	contain	14.53
8875	"	29.25	9476	"	13.46
9000	"	26.00	9513	"	12.40
9054	"	25.37	9545	"	11.56
9166	"	22.07	9573	"	10.82
9255	"	19.54	9597	"	10.17
9326	"	17.52	9619	"	9.60
9385	"	15.88	9692	"	9.50

According to Dalton, (*New System of Chem.*, ii. 422,) the following are the strengths of solutions of ammonia of different specific gravities, as also their respective boiling-points:—

Specific Gravity.	Grains of Ammonia in 100 grains of the liquid.	Boiling Points.	Volumes of gas in one volume of liquid.
.850	35.3	26°	494
.860	32.6	38	456
.870	29.9	50	419
.880	27.3	62	382
.890	24.7	74	346
.900	22.2	86	311
.910	19.8	98	277
.920	17.4	110	244
.930	15.1	122	211
.940	12.8	134	180
.950	10.5	146	147
.960	8.3	158	116
.970	6.2	173	87
.980	4.1	187	
.990	2.0	196	28

The usual state in which ammonia is employed is in aqueous solution, both in chemistry and medicine. This solution bears the name of *Liquor Ammonia* in the *London Pharmacopæia*. It may be obtained by passing the gas into water in a proper apparatus, or by distilling over the water and gas together. Dr. Turner recommends for this process, the use of equal parts of sal-ammoniac and well-burned quick-lime: the lime is slaked by

the addition of water, and as soon as it has fallen into powder, placed in an earthen pan, and covered, till quite cold, then mixed with the powdered sal-ammoniac and put into a proper retort and heated as long as it gives out gas, which should be conducted by means of a safety-tube of Welter into a quantity of distilled water, equal to the weight of the salt employed. The specific gravity of the solution of ammonia so obtained is .936. (*Elem. of Chem.* 5th ed., 384.)

The following process, recommended by Mr. R. Phillips, answers well. On 9 ounces of well-burned lime pour half a pint of water, and when it has remained in a well-closed vessel for about an hour, add 12 ounces of hydrochlorate of ammonia in powder and three pints and a half of boiling water; when the mixture has cooled, pour off the clear portion, and distil from a retort 20 fluid ounces. The specific gravity of this solution, which is sufficiently strong for most purposes, is 0.954. (*Remarks on London Pharmacopœia*, p. 34.) The specific gravity of the official solution directed in the *Pharmacopœia*, is 0.960.

Liquid ammonia, as this aqueous solution of it is commonly called, should be preserved in well-stopped glass bottles, since it loses ammonia and absorbs carbonic acid, when exposed to air. When heated, ammonia is rapidly given off by it; when concentrated, it requires to be cooled to -40° before it congeals, and then it is apparently inodorous, and of a gelatinous appearance. If a piece of ice be introduced into a jar of ammonia standing over quicksilver, it melts with great rapidity, and liquid ammonia is produced.

A pure and strong solution of ammonia is a bad conductor of electricity, but it becomes a conductor when sulphate of ammonia is dissolved in it, and then, if submitted to electrolytic action, Faraday found that nitrogen was evolved at the anode, and hydrogen at the cathode, the ratio of the volume of the former to that of the latter varying, but being as 1 to about 3 or 4. This result seemed to indicate that the electric current had decomposed the ammonia, and that the nitrogen had been determined towards the positive electrode. But when the electricity used was measured out by the voltmeter, it was found that the hydrogen obtained was exactly in the proportion which would have been supplied by decomposed water, whilst the nitrogen had no certain or constant relation whatever; and upon further experiment, that the water only was electrolyzed and that the nitrogen at the anode was a secondary result, depending upon the chemical action of the nascent oxygen (determined to that surface by the electric current) upon the ammonia. No experiment has hitherto shown any tendency of nitrogen under the influence of the electric current to pass in either direction along its course. (*Phil. Trans.*, 1834, p. 95.)

Dr. Henry (*Phil. Trans.*, 1809) first observed that a mixture of ammonia and oxygen might be fired by an electric spark, and this property furnishes a means of analyzing the alkaline gas. Electricity also decomposes ammoniacal gas. If a succession of electrical sparks be passed through a small portion of the gas confined in a proper tube over quicksilver, it will increase to about twice its original bulk, and lose its easy solubility in water. If the gas thus expanded be mixed with from one-third to one-half its bulk of oxygen, and an electric spark passed through the mixture, an explosion takes place, attended by considerable

diminution. Note the amount of the diminution, divide it by 3, and multiply the product by 2. The result shows the quantity of hydrogen; for 2 measures of hydrogen are saturated by 1 of oxygen. Thus, suppose 10 measures of ammonia, expanded by electricity to 18, and that, after adding 8 measures of oxygen gas, we find the whole (=26 measures) reduced by firing to 6 measures, the diminution will be 20. Then $20 \div 3 = 6.66$; and $6.66 \times 2 = 13.32$ measures of hydrogen gas from 10 of ammonia; and $18 - 13.32 = 4.68$ for the nitrogen gas contained in the product of electrization. Therefore, 10 measures of ammonia have been destroyed and expanded into 13.32 measures of hydrogen and 4.68 of nitrogen gas. (HENRY'S *Elements*, 7th ed., vol. i. p. 233.)

Nitrogen.	Hydrogen.	=	Ammonia.
14	1		
	Hydrogen.		
	1		17
	Hydrogen.		
	1		

It appears from the above, and from the prior experiments of Berthollet, that 1 volume of ammonia is resolved by decomposition into 2 volumes of a mixture of hydrogen and nitrogen, consisting of 3 volumes of hydrogen and 1 volume of nitrogen; hence the annexed diagrams will represent the composition and volume of ammonia.

Such being the volumes of the gases, it follows that if we add the specific gravity of nitrogen to thrice the specific gravity of hydrogen and divide the product by 2, we ought to obtain the specific gravity of ammonia;

$$\begin{array}{rcl} \text{Specific Gravity of nitrogen} & \dots & = 0.972 \\ \text{,, hydrogen} & \dots & 0.0694 \times 3 = 0.208 \end{array}$$

Or,

$$1.180 \div 2 = 0.590$$

50	Cubic inches of nitrogen weigh	15.08
150	,, hydrogen	3.19
100	,, ammonia	18.27

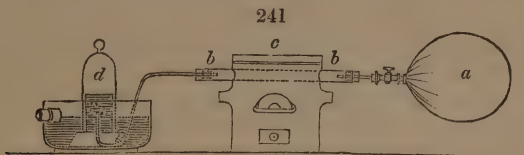
Ammonia, therefore, is a compound of

				Berthollet.	Vols.	Sp. Gr.	100 Cub. In.		
Nitrogen	1	..	14	..	82.35	82.35	1	0.972	30.16
Hydrogen	3	..	3	..	17.65	17.65	3	0.208	6.40
Ammonia	1		17		100.00	100.00	2	0.590	18.28

When ammonia is detonated with excess of oxygen, a portion of nitric acid seems always to be formed: indeed, according to Bischof, this acid is more or less formed in all cases of its combustion with oxygen. He found the limits of combustibility with oxygen to be, on the one hand, 1 ammonia and 0.6 oxygen; and, on the other, 1 and 3.17 by volume.

Ammonia, like most of the compounds of nitrogen, is not permanent at a red heat, and is consequently decomposed when passed through a red-hot tube. If passed over a coil of iron or copper wire in a red-hot porcelain tube, the metals become brittle, but their weight is not altered

According to Thenard (*Ann. de Chim.*, LXXV. 61), when any of the five following metals are enclosed in the tube, they promote the decomposition of ammonia at a temperature below that which it requires *per se*, in the following order: iron, copper, silver, gold, platinum. In all these cases the gas suffers expansion, and is resolved into hydrogen and nitrogen gases, in the above-stated proportions; it furnishes a singular instance of change of properties in consequence of chemical combination. (*a* is a bladder filled with ammonia, which may be passed through the iron tube *b*, placed in the furnace *c*; the gas is decomposed, and hydrogen and nitrogen may be collected over the water in *d*.)



Ammonia is also decomposed when passed over black oxide of manganese, heated red-hot in a porcelain tube; the results, which are *water* and *nitrous acid*, were first observed by the Rev. J. Milner. (*Phil. Trans.*, vol. LXXIX.) *Nitrate of ammonia* is also often formed. Passed through a porcelain tube containing red-hot charcoal, ammonia forms a portion of hydrocyanic acid.

Ammonia is produced synthetically during the decomposition of many animal substances; it is also formed during the violent action of nitric acid upon phosphorus and some of the metals; and by moistened iron-filings exposed to an atmosphere of nitrogen: in these cases the nascent gases unite so as to form a portion of ammonia. Common rust of iron formed by the exposure of iron to a damp atmosphere, also generally contains traces of ammonia. According to Dr. Hare, ammonia is also synthetically formed by the action of spongy platinum on a mixture of 2 volumes of nitric oxide and 5 of hydrogen. For such experiments he recommends platinated asbestos, formed by dipping asbestos into a solution of chloride of platinum and exposing it to a red-heat. There are some other anomalous cases of the evolution and apparent production of ammonia, which are not easily explained, but which have been enumerated and commented upon by Mr. Faraday, in a paper published in the *Quarterly Journal* (vol. xix. p. 16).

Ammonia combines with the acids, and produces a class of salts which, with very few exceptions, are soluble in water, and which evolve the odour of ammonia when mixed with lime or with pure potassa. These salts are, for the most part, entirely dissipated, and, generally speaking, decomposed by heat. Ammonia mixed with the gaseous acids condenses them into white pulverulent compounds; it combines either with half its volume, or with an equal volume, or with two volumes of the acid. The same combination ensues when the volatile acids are brought near free ammonia; and in this way very minute quantities of ammonia may be discovered, by dipping a glass rod into hydrochloric, nitric, or acetic acid, and bringing it near any liquid or substance supposed to evolve ammonia, which will be immediately recognised by white

fumes. The constitution of ammoniacal salts involves many important theoretical considerations respecting the nature of ammonia, which will presently be adverted to.

AMMONIA AND CHLORINE.—When these gases are mixed, a partial decomposition of the former ensues. On mixing 15 parts of chlorine and 40 of ammonia, 5 parts of nitrogen are liberated, and *hydrochlorate of ammonia* is formed. If the gases be perfectly dry, considerable heat is evolved, and a flame is perceived to traverse the vessel in which the experiment is made. This combustion of ammonia in chlorine is well shown by annexing to the beak of a small tubulated retort, containing a mixture of hydrochlorate of ammonia and lime, a bent tube, not too small, the extremity of which terminates in a bottle containing chlorine; on heating the contents of the retort, ammonia is evolved, and as it issues from the tube into the chlorine, it inflames, and continues to burn with a pale lilac flame, producing hydrochlorate of ammonia, and evolving nitrogen. Dr. Thomson employed *chloride of lime* to decompose ammonia, by mixing it with hydrochlorate of ammonia, and collecting the evolved nitrogen. When solutions of chlorine and ammonia are mixed, an effervescence ensues, nitrogen gas is evolved, and hydrochlorate of ammonia formed; and when gaseous chlorine is transmitted in successive bubbles into a strong solution of ammonia, each produces a slight explosion attended by a flash of light. (See p. 405.)

The best mode of showing the mutual action of ammonia and chlorine in solution, is to pour into a tube, about two feet long and half an inch in diameter, sealed at one end, a strong aqueous solution of chlorine, to within about two inches of the top; then gradually to pour upon it liquid ammonia, so as to fill the tube, which is to be closed by the thumb, and inverted into water; the solution of ammonia then rises through that of chlorine, and is decomposed with effervescence, nitrogen being evolved, and hydrochlorate of ammonia retained in solution.

AMMONIA AND CHLORIC ACID. ($A + C'$.) *Chlorate of ammonia* is formed by saturating chloric acid with carbonate of ammonia. It forms very soluble acicular crystals, of a sharp taste, which detonate when thrown upon hot coals. It probably consists of one proportional of each of its components, or 17 ammonia + 76 chloric acid: but its composition has not been experimentally determined. (VAUQUELIN, *Ann de Chim.*, xcv. 97.)

AMMONIA AND HYDROCHLORIC ACID. **HYDROCHLORATE OF AMMONIA.** **MURIATE OF AMMONIA.** **SAL AMMONIAC.** ($n + 3h$) + ($h + c$), or ($A + hc'$), or $NH_3 + HC$ (*Hypothetical CHLORIDE OF AMMONIUM*).—This salt may be produced, directly, by mixing equal volumes of ammonia and hydrochloric acid gases, when an entire condensation ensues. The specific gravity of ammonia compared with hydrochloric acid is as 8.5 to 18.5; therefore, hydrochlorate of ammonia consists of

Ammonia.	Hydrochloric Acid.	Bucholz.			
8.5	18.5	or, { Ammonia . . .	1 . . 17 . .	31.5 . .	31
		{ Hydrochloric acid	1 . . 37 . .	68.5 . .	69
			<hr/> 1	<hr/> 54	<hr/> 106.0
					<hr/> 100

This salt was formerly imported from Egypt, where it was obtained by burning the dung of camels (see PARKES'S *Essays*, ii. 437); it is now abundantly prepared on the continent and in this country, chiefly by the decomposition of *sulphate of ammonia* by chloride of sodium or of magnesium. When obtained by evaporation from its solution in water, it forms octoëdral, cubic, and plumose crystals; but, in commerce, it usually occurs, as procured by sublimation, in colourless and translucent cakes, hard, and somewhat elastic, specific gravity 1.45, and very slightly deliquescent: in this compact state it requires for solution about an equal weight of water at 212°, and three times its weight at 60°, cold being produced during its solution; it also dissolves in alcohol: when heated it sublimes without decomposition in the form of white vapour, and may be even passed through a red-hot porcelain tube without change. It is, however, decomposed when transmitted over ignited iron or copper-wire.

Sal-ammoniac is used in the arts for a variety of purposes, especially in certain metallurgic operations. It is used in tinning, to prevent the oxidation of the surface of copper; and small quantities are consumed by dyers. Dissolved in nitric acid, it forms the *Aqua Regia* of commerce, used for dissolving gold, instead of a mixture of nitric and hydrochloric acids. It is decomposed by the fixed alkalis, and by the alkaline earths.

Native sal-ammoniac occurs massive and crystallized, in the vicinity of volcanoes, and in the cracks and pores of lava near their craters. It has thus been found at Etna, and at Vesuvius, in the Solfaterra near Naples, and in some of the Tuscan lakes. An efflorescence of it is sometimes seen upon pit-coal. Its colour varies, from the admixture of foreign matter, and it is frequently yellow from the presence of sulphur. It is said that considerable quantities of native sal-ammoniac are also found in the country of Bucharia, where it occurs with sulphur in rocks of indurated clay. The ancients, according to Pliny, called this salt *ammoniac*, because it was found near the temple of Jupiter Ammon, in Africa. It has been detected by Dr. Marcet in sea-water. (*Phil. Trans.*, 1822, p. 454.)

AMMONIA AND IODINE.—The mutual action of iodine and ammonia was first studied by Colin. (*Ann. de Chimie*, xci. 262.) Iodine absorbs dry ammoniacal gas, and produces a viscid compound, at first of a metallic appearance, but becoming deep brown and more liquid by excess of ammonia. Added to water this liquid produces a crimson-coloured solution, and yields iodide of nitrogen: it is also soluble in alcohol, and acts more powerfully on organic matter than pure iodine. Exposed to air it ultimately leaves a pale-brown powder, powerfully detonating, and exhibiting a bright light at the moment of explosion. Landgrebe, who has ascertained these facts (POGGENDORFF'S *Annalen*, xiv. 539), considers this as a distinct iodide. It detonates at the temperature of about 80°. The action of iodine on liquid ammonia has been already described. Berzelius regards the iodide of ammonia as an hydriodate of iodide of nitrogen and of ammonia. Bineau states that 100 parts of iodine absorb 20.4 of ammonia, which is in the proportion of 2 atoms of iodine and 3 atoms of ammonia. (*Ann. de Ch. et Ph.*, Lxvii. 228.)

IODATE OF AMMONIA ($i + 5o$) + ($h + 3n$) is obtained by saturating iodic acid with ammonia. It forms small crystals, sparingly soluble in water; it deflagrates, when thrown upon hot coals, with a pale violet flame; heated highly in a tube it explodes, and is decomposed into oxygen, nitrogen, water, and iodine. Its composition has not been experimentally ascertained.

HYDRIODATE OF AMMONIA. ($h + 3n$) + ($h + i$) or ($A + hi$). In a former paragraph the action of iodine on ammonia has been stated to produce a portion of hydriodate of ammonia: this compound may be directly formed by mixing equal volumes of hydriodic and ammoniacal gases; or by saturating liquid hydriodic acid by carbonate of ammonia: it forms very soluble and deliquescent cubic crystals, which are anhydrous, and volatile in close vessels without decomposition. Its aqueous solution dissolves iodine. (GAY LUSSAC, *Ann. de Chim.*, xci.) Hydriodate of ammonia consists of

Ammonia	1	.	17	.	12
Hydriodic acid	1	.	126	.	88
<hr/>					<hr/>		<hr/>		<hr/>
Hydriodate of ammonia					1		143		100

AMMONIA AND BROMINE act on each other with the evolution of nitrogen, and form *hydrobromate of ammonia*; but no *bromide of nitrogen*.

BROMATE OF AMMONIA has not been examined.

HYDROBROMATE OF AMMONIA. ($A + hb$) is a volatile prismatic salt, becoming yellow and slightly acid by exposure to air. It is constituted of equal volumes of gaseous hydrobromic acid and ammonia.

HYDROFLUATE OF AMMONIA. ($A + hf$). According to Berzelius, the neutral hydrofluante is best obtained by heating in a platinum crucible a mixture of one part of hydrochlorate of ammonia with 2.25 parts of fluoride of sodium, both in fine powder: the cover of the crucible should be inverted, and contain water, to be replaced as it evaporates, so as to prevent its temperature exceeding 212° . A gentle heat sublimes the salt, which attaches itself in small prismatic crystals to the cool cover. If the salts were moist, ammonia is evolved, and an acid salt obtained. *Hydrofluante of ammonia* is permanent in the air, readily soluble in water, and less so in alcohol. At a high temperature it melts and sublimes; it corrodes glass, and its solution furnishes a ready means of etching upon it; it absorbs ammonia, but does not retain it when sublimed. When its solution is evaporated, ammonia escapes, and a remarkably deliquescent *bihydrofluante of ammonia*, imperfectly crystallizable, remains.

HYPONITRITE OF AMMONIA ($A + \tilde{n}$) is obtained when neutral hyp-nitrate of lead is decomposed by sulphate of ammonia. Its solution is decomposed by a very gentle heat, and evolves nitrogen; but it remains neutral. Exposed to spontaneous evaporation in a dry atmosphere, an irregularly crystallized mass is obtained, which melts, and is decomposed when heated, being resolved into nitrous oxide, water, and ammonia. (BERZELIUS.)

AMMONIA AND NITRIC ACID; NITRATE OF AMMONIA. $(n + 3h) + (n + 5o)$ or $(A + N')$. (*Hypothetical* NITRATE OF OXIDE OF AMMONIUM.) This salt may be procured by the direct union of ammonia with nitric acid; or more easily, by saturating dilute nitric acid with carbonate of ammonia. It has been mentioned as the source of *nitrous oxide*, and when carefully heated it is entirely resolved into that gas and water. Exclusive of water, nitrate of ammonia consists of

Ammonia	.	1	.	17	.	23.9
Nitric acid	.	1	.	54	.	76.1
		1		71		100.0

The decomposition of this salt by heat, and its resolution into nitrous oxide and water, furnishes a good illustration of the theory of definite proportionals, both in volumes and weights; the elements of *nitrate of ammonia* are, 2 atoms of nitrogen, 5 of oxygen, and 3 of hydrogen; and their respective *volumes* are represented in the annexed diagram.

Nitrous oxide consists of 1 proportional of nitrogen $= 14 + 1$ of oxygen $= 8$; hence the 2 proportionals of nitrogen in the salt (1 in the acid, and 1 in the ammonia) will require 2 of oxygen to produce *nitrous oxide*, and the remaining 3 of oxygen will unite to the 3 of hydrogen, to form *water*; and accordingly *nitrous oxide* and *water* are the only possible results; so that the elements after the decomposition of the salt, are arranged as in the opposite diagram:

or, represented by symbols, $(n + 5o) + (n + 3h)$ become $2(n + o)$ and $3(h + o)$.

Nitrate of ammonia has long been known, and was formerly called *Nitrum flammans*, in consequence of its rapid decomposition with a slight explosion when heated to about 600° . It differs in form according to the manner in which its solution has been evaporated; if at a temperature below 100° , its crystals are six-sided prisms terminated by six-sided pyramids; if boiled down, its crystals are thin and fibrous; it is deliquescent, and soluble in twice its weight of water at 60° , and in

NITRATE OF AMMONIA.

Nitric Acid. 54		Ammonia. 17	
Nitrogen.	Oxygen.	Nitrogen.	Hydrogen.
14	8	14	1
	8		1
	8		1
	8		1
	8		1

Two proportionals of Nitrous Oxide.		Three proportionals of Water.	
Nitrogen.	Oxygen.	Hydrogen.	Oxygen.
14	8	1	8
14	8	1	8
		1	8

its own weight at 212° . Its taste is acrid and bitter. It cannot exist without elementary water. According to Berzelius, the *prismatic* variety affords 11.232 per cent.; hence it may be considered as containing

Anhydrous nitrate of ammonia ?	1	71	88.7
Water	1	9	11.3
	1	80	100.0

AMIDOGEN. ($n + 2h$.) AMMONIUM. ($n + 4h$.) In the preceding notice of some of the ammoniacal salts we have considered them, in respect to the oxyacids, as similarly constituted to the metallic salts generally; ammonia appearing to act the part of a metallic oxide, and uniting to the acid to constitute a salt. But the anhydrous acids cannot thus be combined; and one atom of water is essential to the composition of all the salts of ammonia with the oxyacids. Again, we have found that when chlorine and its analogues combine with ammonia, nitrogen is evolved, and a salt is formed in which a hydracid is presumed to have united with remaining undecomposed ammonia; in short, that the same ultimate result is obtained as if ammonia and the hydracid had been directly combined, excepting that in the latter case, no evident decomposition either of the ammonia or acid has ensued. When we come to examine, in a subsequent chapter, the constitution of salts, we shall find that ammoniacal salts present other discrepancies and peculiarities when ammonia is viewed as their base, but that they may be assimilated, if ammonia be considered as the hydruret of a hypothetical base, composed of an atom of nitrogen combined with two atoms of hydrogen, and represented therefore by the symbol ($n + 2h$.) To this hypothetical body, for it has not yet been isolated, the name *amidogen*, or *ammogen*, has been given, and it is assumed that it combines in two proportions with hydrogen, forming *ammonia*, and *ammonium*; but ammonium, like amidogen, has not been separately obtained. The following, therefore, upon this hypothesis, are the compounds of nitrogen with hydrogen:—

Amidogen	{ Nitrogen . . 1 . . 14 Hydrogen . . 2 . . 2 }	or ($n + 2h$).
Ammonia	{ Nitrogen . . 1 . . 14 Hydrogen . . 3 . . 3 }	or ($n + 3h$).
Ammonium	{ Nitrogen . . 1 . . 14 Hydrogen . . 4 . . 4 }	or ($n + 4h$).

It is obvious therefore that amidogen may be considered as the direct or primary combination of nitrogen and hydrogen, and ammonia and ammonium as its two hydrurets, ammonia being ($n + 2h$) + h , and ammonium, ($n + 2h$) + $2h$.

It is assumed that in the ammoniacal salts of the oxyacids an atom of water ($h + o$) is always present, and consequently that they really are salts of oxide of ammonium, the elements of the water being concerned in converting the ammonia into oxide of ammonium; for it is clear ($n + 3h$) + $h + o$ may be regarded as ($n + 4h + o$). In

reference, therefore, to this view, nitrate of ammonia will be a nitrate of oxide of ammonium; for assuming the nitric acid to be a compound of one atom of anhydrous nitric acid and one atom of water, $(n + 5o) + (h + o)$, in which state it must be to form the salt, it is then clear that nitrate of ammonia will be $(n + 5o) + (n + 3h) + (h + o)$, and that these elements will be equivalent to $(n + 5o) + (n + 4h + o)$.

Again, as regards the combination of the hydrochloric acid with ammonia, and the supposed formation of hydrochlorate of ammonia, this salt, in reference to the preceding statement, must be regarded as a chloride of ammonium, for the elements of ammonia $(n + 3h)$ and of hydrochloric acid $(h + c)$, are equivalent to those of ammonium $(n + 4h)$ and chlorine (c) . The further illustrations of the ammonium theory, as it has been called, and the supposed proofs of the existence of amidogen will be given afterwards.

ATMOSPHERIC AIR.

THE composition of the *atmosphere* has been frequently alluded to in the preceding pages, and now that we are acquainted with its essential elements, nitrogen and oxygen, it will be useful to consider its nature and properties somewhat more in detail.

The atmosphere is a thin, transparent, invisible, and elastic fluid, which surrounds and revolves with our planet, and reaches to a considerable height above its surface, probably between forty and fifty miles.

That air is a *ponderous* body, was first suspected by Galileo, who found that a copper ball, in which the air had been condensed, weighed heavier than when the air was in its ordinary state of tension. The fact was afterwards demonstrated by Torricelli, whose attention was drawn to the subject by the attempt of a well-digger at Florence to raise water by a sucking-pump to a height exceeding 33 feet. It was then found that the *pressure of the atmosphere*, and not Nature's abhorrence of a vacuum, was the cause of the ascent of the water in the pump-pipe, and that a column of about the height mentioned, was sufficient to equipoise the atmosphere, which, at the level of the sea, presses with a weight of about *fifteen pounds on every square inch of surface*, and is capable of supporting a column of water about 34 feet high. Comparing the specific gravity of mercury with that of air and water, Torricelli inferred that if a column of air one inch square and as high as the atmosphere, weighed 15 pounds, and a column of water 34 feet high and an inch square, weighed also 15 pounds, the height of a similar column of mercury would be about 30 inches; he accordingly, in 1643, filled a glass tube, three feet long and closed at one end, with mercury, and inverted it in a basin of the same fluid; he found that the mercury fell about six inches, so that the atmosphere counterbalanced a column of *mercury* 30 inches in height. The empty space, in the upper part of the tube, has hence been called the *Torricellian vacuum*, and is nearly the most perfect that can be formed. Paschal and Torricelli afterwards observed that, upon ascending a mountain, the mercury fell in the tube, because there was less air above to press upon the surface of the metal in the basin; and thus a method of *measuring the heights of mountains by the*

barometer, as the instrument is now called, was devised. Sir Henry Englefield constructed a barometer expressly for these investigations, the mode of using which is described in the *Journal of Science and the Arts*, vol. v., p. 229. Such instruments are now commonly called *Mountain Barometers*.

The barometer indicates, by its rise and fall, a corresponding change in the pressure of the atmosphere. At the surface of the earth the *mean* density or pressure is considered equal to the support of a column of *mercury* 30 inches high, which would give a pressure upon every square inch of about 15 lbs.*

			Inches.
At 1000 feet above the surface the column falls to			28·91
2000	"	"	27·86
3000	"	"	26·85
4000	"	"	25·87
5000	"	"	24·93
1 mile	"	"	24·67
2	"	"	20·29
3	"	"	16·68
4	"	"	13·72
5	"	"	11·28
10	"	"	4·24
15	"	"	1·60
20	"	"	0·95

At a height of 2·705 miles, = 11,556 feet, one volume of the atmosphere would expand into two, its calculated density being diminished at that height by one-half; the density is again halved at every 2·7 miles additional elevation, as in the following table.

Height above the sea in miles.	Volume.
0	1
2·705	2
5·410	4
8·115	8
10·820	16
13·525	32
16·230	64
18·935	128

It has been ascertained that the temperature of the atmosphere diminishes about 1° for every 350 feet of ascent, the cause of which is partly referable to the increased capacity of air for heat in proportion as its density diminishes, and partly to the circumstance that the atmosphere is chiefly heated by the earth. The line of perpetual congelation gradually descends from the equator to the poles. At 0° latitude it is stated to be 15200 feet; at 60° , 3818; and at 75° , only 1000 feet.

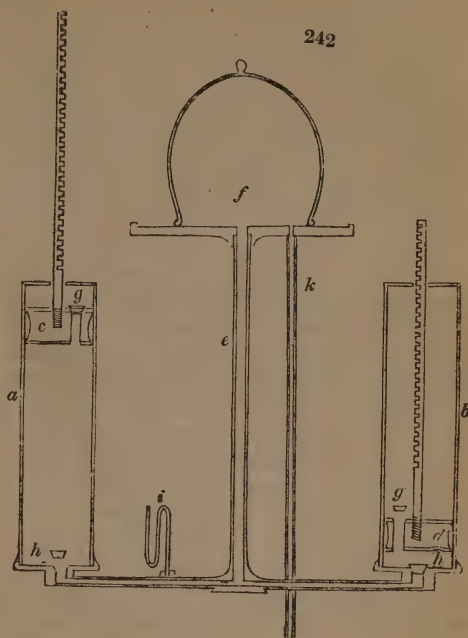
THE MECHANICAL PROPERTIES OF THE AIR are best illustrated by the *air-pump*, the construction of which much resembles that of the com-

* This is equal to a column of *water* of between 33 and 34 feet in height, and accordingly in all ordinary cases, the requisite length of the tube prevents the construction of *water-barometers*, but their great rise and fall, as compared with the mercurial column, and the singular facility with which they fluctuate with atmospheric changes, renders

observations with such instruments curious and instructive. A water-barometer was put up, in the year 1832, in the Hall of the Royal Society at Somerset House, under the direction of Mr. Daniell, of which an interesting description will be found in the *Philosophical Transactions* for that year.

mon pump for raising water, excepting that all the parts are more accurately and nicely made, the object being to exhaust the air as completely and expeditiously as possible. The annexed sketch (figure 242,) will give an idea of the operation of the common air-pump.

The annexed sketch (figure 242,) will give an idea of the operation of the common air-pump. *ab* are cylinders, into which the sliding-pistons *cd* are accurately fitted: *e* is a tube issuing from the bell-glass placed upon a brass plate *f*, and entering the lower part of the cylinders at *hh*, where are valves opening upwards. In each piston is also a valve opening upwards at *gg*. The cylinder *a* represents the piston in the act of being drawn up. By elevating the piston *c*, an attempt will be made to form a vacuum underneath it; but a portion of the air,



in consequence of its elasticity, will pass out of the bell *f*, along the tube *e*, and elevating the valve *h*, will fill the space below the piston, the valve *g* being kept closed by the weight of the incumbent atmosphere. In the cylinder *b* the piston is represented in the act of depression, the valve *h* therefore is forced down upon the orifice, which it perfectly closes; and the air, confined between it and the piston, now makes its escape by the piston-valve *g*, which is accordingly open, so that at every stroke of the pump a portion of air is withdrawn from the receiver *f*.

With this air-pump it is obviously impossible to obtain more than an imperfect vacuum in the receiver *f*, for the valves can only act by the elasticity of the remaining air; and, accordingly, if a barometer be placed under the receiver, the mercury will never attain a level in the tube and basin, but will always indicate a degree of pressure, as is shown by the small syphon gauge at *i*; and if a tube three feet long (*k*) have its upper end opening into the receiver, and its lower end plunged into a basin of mercury, the mercury will never rise so high as in the common barometer, where the vacuum above it is more perfect, but will indicate the pressure of a remnant of air in the receiver. The syphon gauge, and the barometer-gauge as applied at *k*, are very useful appendages to the air-pump, as showing the degree of exhaustion, and its permanence.

The operation of the pump in removing air, and the mechanical properties of the atmosphere, may be shown by a variety of experiments. Its pressure is illustrated by the force with which the bell-glass is pressed

down upon the plate of the pump; the *absence of its buoyancy*, by the descent of a guinea and a feather at the same time in the exhausted receiver; and by the preponderance of the larger of two bodies which balance each other in the open air. The *want of resistance* in the exhausted receiver is also shown by the equal duration of the motion of two fly-wheels, with their plates placed in different directions. The *elasticity* of the air is illustrated by the action of the pump itself, or by the distension which a flaccid bladder suffers during the removal of the external air, when placed under the receiver.

The extreme elasticity of the air, and the changes of bulk which it is constantly sustaining under variations of pressure and of temperature, have been already partially adverted to. The general law of its compression was originally developed by Boyle in 1662, and afterwards investigated by Mariotte. They found that the volume of air, and all other elastic fluids retaining that state, was inversely as the pressures acting upon them. Thus a volume of air = 100 under any given pressure, will be diminished to 50 when that pressure is doubled; and expanded to 200 when the pressure is diminished by one half. From the experiments of Oersted (*Edinburgh Journal of Science*, iv.), this law applies under very high pressures; indeed, till liquifaction is effected. We have, however, no evidence of the liquifaction of atmospheric air under any pressure, Mr. Perkins's experiments upon that subject (*Phil. Trans.*) not being conclusive.

SPECIFIC GRAVITY OF AIR.—The specific gravity of atmospheric air, at mean temperature and pressure, that is, the thermometer being at 60° , and the barometer at 30 inches, is usually considered as = 1, being the standard of comparison to which the specific gravities of gases and vapours are referred. In consequence of the interfering causes, and the delicacy of the methods required for the determination of the weight of a given bulk of air, the results of different experimentalists are a little at variance; and accordingly the tables of the specific gravities of æriform fluids, given in different works, are seldom exactly consistent with each other. From the latest experiments of Dr. Prout, 100 cubic inches of pure and dry atmospheric air, at mean temperature and pressure, weigh 31·0117 grains, so that, upon this datum, it is about 815 times lighter than its bulk of water, and 11,065 times lighter than its bulk of mercury. At the temperature of 32° , 100 cubic inches of atmospheric air weigh, according to Dr. Thomson, 32·79 grains. Compared with hydrogen its specific gravity is as 15·2 to 1. In the following table (drawn up by Mr. Daniell) the weight of 100 cubic inches of the lightest and heaviest known forms of matter are contrasted with air and with water in its different states: their specific gravities compared with air and water are also shown.

100 Cubic inches.	Weight in grains.	Sp. gr., air being = 1.	Sp. gr., water being = 1.
Hydrogen	2·138	0·0694	0·0000846
Air	31·000	1·0000	0·0012277
Steam	19·220	0·6240	0·0007611
Ice	23735·000	765·0000	0·9400000
Water	25250·000	814·0000	1·0000000
Platinum	542875·000	17512·0000	21·0000000

DETERMINATION OF THE SPECIFIC GRAVITY OF GASES.—For ascertaining the specific gravity of gaseous bodies, a good air-pump is essentially requisite; a light glass balloon (fig. 243) or flask *b*, and a graduated air-jar *a*, each supplied with stop-cocks, are also required. The stop-cock attached to the flask should be as small and light as possible.

Dr. Henry, in his *Elements of Chemistry*, and Mr. Faraday, in his *Chemical Manipulation*, have given explicit and extended directions for determining the specific gravities of gases, to which the reader is referred, and of which the following is an abstract.

The gases should be retained and collected over mercury, and carefully dried, by exposing them to proper substances for absorbing the aqueous vapour with which they are mixed, and which would sometimes materially affect the accuracy of the result; or they should be taken saturated with moisture, and a correction afterwards made for the weight of the vapour contained in a given bulk of the gas.

Supposing the receiver *a* to be filled with any gas, the weight of which is to be ascertained, screw the cock of the vessel *b* on the plate of an air-pump, and exhaust it as completely as possible, carefully ascertaining by the barometer-gauge of the pump, that it retains its vacuum. The weight of the exhausted vessel is then very accurately taken, even to a small fraction of a grain; and it is screwed upon the cock of the receiver *a*. On opening both cocks, the last of which should be turned very gradually, the gas ascends from the vessel *a*; and the volume which enters into the flask is known by the graduated scale on *a*. On weighing the vessel a second time, we ascertain how many grains have been admitted. If we have operated on common air, we shall find its weight to be at the rate of 31 grains to 100 cubical inches. The same quantity of oxygen gas will weigh 34·60 grains, and of carbonic acid gas 47·3 grains. In these manipulations, care is to be taken not to warm any of the vessels by contact with the hands, from which they should be defended by a glove. On opening the communication between the receiver and the exhausted vessel, if any water be lodged in the air-cock attached to the former, it will be forcibly driven into the latter, and the experiment will be frustrated. This may be avoided by using great care in filling the receiver with water, before passing into it the gas under examination: a small plug of bibulous paper, or of cotton, may also be put into the upper orifice of the stop-cock.

The specific gravity of any gas, compared with common air, is readily known, when we have once determined its absolute weight. Thus, if 100 cubic inches of air weigh 31 grains, and the same quantity of oxygen gas weigh 34·6 grains, we say,

$$31 : 34\cdot6 :: 1\cdot000 : 1\cdot111.$$

The specific gravity of oxygen gas, compared with atmospheric air, will therefore be as 1·111 to 1·000.

We may determine, also, the specific gravity of gases more simply, by weighing the flask, first when full of common air, and again when exhausted; and afterwards by admitting into it as much of the gas under



examination as it will receive, and weighing it a third time. Now, as the loss between the first and second weighing is to the gain of weight on admitting the gas, so is common air, to the gas whose specific gravity we are estimating. Supposing, for example, that by exhausting the flask it loses 31 grains, and that by admitting carbonic acid it gains 47·3; then

$$31 : 47\cdot3 :: 1\cdot000 : 1\cdot527.$$

The specific gravity of carbonic acid is, therefore, 1·527, air being taken at 1·000. And knowing its specific gravity, we can, without any further experiment, determine the weight of 100 cubic inches of carbonic acid; for, as the specific gravity of air is to that of carbonic acid, so is 31 to the number required; or

$$1\cdot000 : 1\cdot527 :: 31 : 47\cdot3.$$

100 cubic inches, therefore, of carbonic acid, will weigh 47·3 grains.

In consequence of the facility with which the bulk of aëriform bodies is altered by variations of pressure and temperature, these must always be taken into account when speaking of their respective volumes: for convenience sake, they are generally therefore reduced to what is termed *mean* pressure and temperature: *mean pressure* being that which sustains 30 inches of mercury in the barometer tube, and *mean temperature* that of 60° of Fahrenheit, or 15° of the Centigrade scale. This, at least, is by far the most convenient thermometric point, though it unfortunately happens that it is not always strictly adhered to; for by Act of Parliament, the temperature at which the specific gravity of spirituous liquors is determined for the purposes of the excise, and that at which the standard weights and measures are adjusted, is 62°.

The following are the rules for the reduction of gaseous volumes to mean pressure and temperature.

First, in respect to *pressure*, (assuming the mean height of the barometer as = 30 inches,) it is obvious that as the mean height of the barometer is to the observed height, so is the observed volume to the volume required. Suppose, for instance, we had measured 100 cubic inches of air at a barometrical pressure of 29 inches, and wished to know what would be its volume at 30 inches, we shall find by the rule of proportion that

Mean height.	Observed height.	Observed volume.	Required volume.
30	: 29	: 100	: 96·6

Or, in regard to weight, suppose that with the barometer at 29 inches, we had found 100 cubic inches of air to weigh 29·9 grains, and wished to know what the weight would be at standard pressure, we shall find by the rule of proportion that

Observed height.	Mean height:	Observed weight.	Required weight.			
29	:	30	:	29·9	:	31

Secondly, in respect to *temperature*, it has been above stated (page 142) that 100 volumes of air at 32° become 137·5 at 212°, the increase being $\frac{37\cdot5}{100}$ th of the original bulk: dividing this by 180, it is found that a volume of air dilates $\frac{1}{4\cdot80}$ th of the volume which it occupied at 32° for every degree of Fahrenheit's scale, and the same law applies to all other aëriform bodies not in contact with any liquid. If, therefore, it be re-

quired to know what volume 100 cubic inches of air at 70° would occupy at 60° , we must bear in mind that it is not $\frac{1}{480}$ th part per degree of the observed volume at 70° , which is to be deducted; but $\frac{1}{480}$ th part of the volume which 100 cubic inches at 70° would occupy at 32° . Now 480 parts of air at 32° , become 481 parts at 33° , and increase one part for every additional degree, so that at 60° they have increased to 508 parts, and at 70° to 518 parts, and thus we have a proportion between the volumes at 60° and 70° by which we can determine the question: for

Volume at 70° .		Volume at 60° .		Cub. in. at 70° .		Cub. in. at 60° .
480 + 38	:	480 + 28	:	100	:	98·069

or, on the other hand, if we wish to know the correct volume at 60° , of 40 cubic inches of air observed at 35° ,

Volume at 35° .		Volume at 60° .		Cubic inches.		Cubic inches.
480 + 3	:	480 + 28	:	40	:	42·07

Again; the weight of 100 cubic inches of air being 31 grains at 60° , the weight of an equal volume at 212° will be found as follows:—

Volume at 212° .		Volume at 60° .		Grains.		Grains.
480 + 180	:	480 + 28	:	31·0	:	23·86

In making the correction for temperature in addition to that for pressure, it matters not which is first applied to the observed volume, as the result will be the same in either case*.

It has already been observed that gas, when standing over water, becomes saturated with aqueous vapour, the quantity being proportional to the temperature. In such cases a part of the observed volume, as well as of the weight, is due to vapour, which therefore must be determined before the actual weight of the gas can be accurately calculated. The following table (FARADAY, *Manipulation*, 2nd edition, p. 376,) exhibits the proportion by volume of aqueous vapour existing in any gas standing in contact with water at the corresponding temperatures and at mean barometric pressure.

40° . . .	·00933	54° . . .	·01533	68° . . .	·02406
41 . . .	·00973	55 . . .	·01586	69 . . .	·02483
42 . . .	·01013	56 . . .	·01640	70 . . .	·02566
43 . . .	·01053	57 . . .	·01693	71 . . .	·02653
44 . . .	·01093	58 . . .	·01753	72 . . .	·02740
45 . . .	·01133	59 . . .	·01810	73 . . .	·02830
46 . . .	·01173	60 . . .	·01866	74 . . .	·02923
47 . . .	·01213	61 . . .	·01923	75 . . .	·03020
48 . . .	·01253	62 . . .	·01980	76 . . .	·03120
49 . . .	·01293	63 . . .	·02050	77 . . .	·03220
50 . . .	·01333	64 . . .	·02120	78 . . .	·03323
51 . . .	·01380	65 . . .	·02190	79 . . .	·03423
52 . . .	·01426	66 . . .	·02260	80 . . .	·03533
53 . . .	·01480	67 . . .	·02330		

By reference to this table, which is founded upon the experiments of Mr. Dalton and Dr. Ure, and includes any temperature at which gases

* I have taken the above equations from Mr. DANIELL'S *Introduction* (§ 154) upon the subject: the rule is frequently misunderstood and therefore misstated. to which I refer for further remarks

are likely to be weighed, the proportions in bulk of vapour present, and consequently of the dry gas, may be easily ascertained. For this purpose the observed temperature of the gas should be looked for, and opposite to it will be found the proportion in bulk of aqueous vapour at a pressure of 30 inches. The volume to which this amounts should be ascertained and corrected to mean temperature. Then the *whole* volume is to be corrected to mean temperature and pressure, and the corrected volume of vapour subtracted from it. This will leave the corrected volume of dry gas. It has been ascertained, in a manner approaching to perfect accuracy, that a cubic inch of permanent aqueous vapour corrected to the temperature of 60° , and a mean pressure of 30 inches, weighs 0.1929 grains. The weight, therefore, of the known volume of aqueous vapour, is now easily ascertained, and this being subtracted from the weight of the moist gas, will give the weight of the dry gas, the volume of which is also known. As an illustration, suppose a gas standing over water had been thus weighed, and that 220 cubic inches at the temperature of 50° Fahr., and barometric pressure of 29.4 inches had entered into the globe and caused an increase in weight of 101.69 grains. By reference to the table it will be found that at the temperature of 50° , the proportion of aqueous vapour in gas standing over water is .01333, which in the 220 cubic inches will amount to 2.933 cubic inches, which, corrected to the temperature of 60° , becomes 2.942 cubic inches. The whole volume corrected to mean temperature and pressure will be found to equal 219.929 cubic inches, from which, if the 2.942 cubic inches of aqueous vapour present be subtracted, it will leave 216.987 cubic inches as the volume of *dry* gas at mean temperature and pressure: 2.942 cubic inches of aqueous vapour weigh .5675 grains, for $2.942 \times 0.1929 = 0.5675$; this subtracted from 101.69, the whole weight leaves 101.1225 grains, which is the weight of the 216.917 cubic inches of dry gas; and by the simple rule of proportion, therefore, it will be found that 100 cubic inches of such gas, when dried, and at mean temperature and pressure, will weigh 46.603 grains.

Mr. Daniell (*Introduction*, § 203) gives the following data for calculating the amount of the correction for moisture. "Suppose we found 100 cubic inches of a gas saturated with vapour, properly corrected for the temperature of 60° , and 30 inches pressure, to weigh 31 grains, and wished to know the equivalent bulk and weight of the dry gas. The observed volume is partly due to the expansion occasioned by the vapour, and this portion will be in the same proportion to the whole as the elasticity of the vapour is to the total elasticity: therefore,

Barom. pressure.	Force of vap. at 60° .	Cubic inches.	Cubic inches.
30.000	: 0.560	: : 100	: 1.86

The volume of the dry gas is therefore $100 - 1.86 = 98.14$ cubic inches. Now this expansion of 1.86 cubic inches may be regarded as so much vapour of the same elasticity as the air diffused through the whole space; and as the specific gravity of such steam compared to air is as 0.620 to 1.000, then

Sp. Gr. of Air.	Sp. Gr. of Steam.	Grains.	Grains.
1	: 0.620	: : 31	: 19.22 = weight of 100 cubic inches of steam;

	Cubic inches.		Grains.		Cubic inches.		Grains.
and	100	:	19.22	:	1.86	:	0.35

which gives the weight of the vapour to be deducted from the total weight: making the weight of 98.14 cubic inches of dry air = $31 - 0.35$ or 30.65.

When it is required to deprive gases of vapour, so as to render them *dry*, they may be slowly passed through a tube about half an inch diameter, and from two to three feet long, containing fragments of fused and dry chloride of calcium, which, by its strong attraction for moisture, effects the desiccation of the gas. A few gases are, however, absorbed by it, in which case fused potassa, or fused carbonate of potassa, duly comminuted, may be substituted. Some gases are conveniently dried by exposing them to a surface of sulphuric acid. (See FARADAY'S *Manipulation*, p. 386.)

COMPOSITION OF THE ATMOSPHERE.—Atmospheric air has already been stated to consist essentially of oxygen and nitrogen: these gases are merely in a state of mechanical mixture, and by no means, as some have supposed, in chemical combination. There are various ways of learning the proportion which the oxygen bears to the nitrogen; and as the relative fitness of the air for breathing has sometimes been considered as depending upon the quantity of oxygen contained in a given volume, the instruments used in these experiments have been called *eudiometers*.

From facts already stated, it is obvious, that if atmospheric air, mixed with a certain quantity of *hydrogen*, be detonated by the electric spark, the absorption will be proportionate to the quantity of oxygen present. When 100 measures of pure hydrogen are mixed with 100 of pure oxygen, the diminution of bulk after detonation will amount to 150 parts; that is, one volume of oxygen condenses two of hydrogen. If we introduce into the graduated detonating tube (fig. 230) 300 measures of common air, and 200 of pure hydrogen, there will remain, after detonation, 314 measures; so that 186 measures will have disappeared, of which one-third may be estimated as pure oxygen: hence 300 parts of air have thus lost 63 of oxygen, or 21 *per cent*.

The general rule, therefore, for estimating the purity of air by hydrogen gas may be stated as follows:—Add to 3 measures of the air under examination 2 measures of pure hydrogen; detonate; and, when the vessel has cooled, observe the absorption; divide its amount by 3, and the quotient is the quantity of oxygen.

This mode of ascertaining the proportion of oxygen in atmospheric air, by detonation with hydrogen, was first resorted to by Volta, and is susceptible of great accuracy, since hydrogen is easily procured almost absolutely pure. An improved detonating tube for these purposes has been described by Gay Lussac. (*Ann. de Chim. et Phys.*, iv. 188.) The simplest form of instrument, however, for detonating gaseous mixtures, is that contrived by Dr. Ure; it consists of a glass syphon with legs nearly of equal length, open and slightly funnel shaped at one extremity, and hermetically sealed and supplied with platinum detonating wires at the other. The sealed leg is graduated by introducing successively equal weights of mercury from a glass measure; 7 ounces and 66 grains troy

occupy the space of a cubic inch, and 34·25 grains represent $\frac{1}{100}$ of that volume. To use this instrument, it is filled with mercury, and inverted in the pneumatic trough; a convenient quantity of the gaseous mixture is introduced, and having applied a finger to the orifice, the tube is removed and inverted so as to transfer the gas to the sealed leg, where its quantity is very accurately measured; we then pour a portion of mercury from the open end of the tube, so as to leave a space of about two inches, and closing the aperture with the thumb, detonate by the electric spark: the included portion of air serves as a spring, and, on withdrawing the thumb, the change of bulk is read off, having previously added mercury, so as to bring it to a level in both legs of the syphon. Any liquid or solid that is required, may then be passed up into the closed end for the analysis of the residuary gas. (*Edin. Phil. Trans.*, 1818.)

The action of *spongy platinum*, already mentioned (p. 386), may be resorted to, to effect the union of oxygen and hydrogen in eudiometrical experiments; or, the air under examination may be mixed with its bulk of pure hydrogen, and two or three of the small balls, composed of spongy platinum and clay, thrown up into the mixture standing over mercury; in the course of an hour or two, when the diminution of bulk has attained its maximum, and the vessel has cooled, the residuary gas is carefully measured, and one-third of its loss of bulk is = to the oxygen.

Scheele, in his eudiometrical experiments, employed *sulphuret of potassium*, the solution of which absorbs oxygen, as may be shown by agitating it with atmospheric air in a graduated glass tube. In this experiment the nitrogen remains unaltered. The *eudiometric tubes* of Dr. Hope (*Nicholson's Journal*, vol. iv.) and Dr. Henry (*Elements*, vol. i. p. 149), as represented in the marginal wood-cuts (fig. 244 and 245), are convenient for such experiments by absorption. The former consists of a small bottle, holding about three ounces, into which the graduated glass tube *a* is carefully fitted by grinding. It also has a ground stopper at *b*.



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To use it, the phial is filled with the solution of the alkaline sulphuret, and the tube *a*, containing the air to be examined, fitted into its place. After inverting and agitating the instrument, the stopper *b* may be opened under water, and the absorption is shown by the rise of the fluid in the tube. For the glass-bottle, Dr. Henry substituted the elastic gum-bottle *b* (fig. 245), in the neck of which a short piece of glass tube is secured, into which the tube *a* is fitted by grinding. In the *Philosophical Transactions* for 1807, Mr. Pepys has described a modification of this eudiometer, which may be often advantageously employed in delicate experiments, and by which an absorption of a thousandth part of the gas under examination may be measured.

When *nitric oxide gas* and atmospheric air are mixed, there is a production of nitrous acid, in consequence of the union of oxygen with the oxide; and if the mixture be made over water, an absorption proportional

to the quantity of nitrous acid formed ensues. Upon this principle nitric oxide may be used in eudiometrical experiments; and, if proper precautions be attended to, it furnishes tolerably accurate results. Priestley and Cavendish, (*Phil. Trans.*, 1783,) availed themselves of this mode, and Dalton has offered some remarks upon its relative accuracy (*Phil. Mag.*, vol. xxviii.) The most certain results are obtained by adding to 100 parts of the atmospheric air, previously introduced into a small beer-glass, an equal volume of nitric oxide gas. The mixture may be gently agitated, and in two or three minutes carefully decanted into a graduated tube, when it will be found, provided the nitric oxide be pure, that 84 measures have disappeared: of which one-fourth, or 21 measures, are oxygen. Sir H. Davy suggested the use of a *solution of protosulphate of iron, impregnated with nitric oxide gas*, for the absorption of oxygen; it may be employed in the same way as the alkaline sulphuret.

If a stick of *phosphorus* be confined in a portion of atmospheric air, it will slowly absorb the oxygen present. The rapid combustion of the same substance may also be conveniently resorted to. For this purpose a small piece of phosphorus may be introduced into the bulb of the tube *a* (fig. 246), containing a given measure of the air to be examined, confined over mercury, which, to prevent loss by expansion, should be suffered to occupy about half the tube, or to stand at *b*. The phosphorus may then be inflamed, and distilled through the air in the tube; and when the combustion is over, and the tube cold, the residuary air may be transferred for measurement. These eudiometrical methods were used by Lavoisier, Berthollet, and Seguin, (*Annales de Chimie*, tom. ix. and xxxiv.,) and are both susceptible of accuracy; and a loss of volume, nearly = 21 per cent. of the atmospheric air, will invariably be found to have occurred.



Lastly, Gay Lussac has recommended the use of slips of copper moistened with hydrochloric acid, for the removal of oxygen from the air; Saussure has used thin turnings of clean metallic lead, which when agitated with a little water in the contact of air, absorbs its oxygen, and forms hydrated oxide of lead: and Berzelius employs the liquid amalgam of lead and mercury for the same purpose. Of these various processes, detonation with, or absorption by, hydrogen, and the action of burning phosphorus, are those which are usually resorted to, and are most precise and easily performed.

By experiments thus conducted, it has been found that the composition of the atmosphere is extremely uniform in all parts of the world, and at all heights above its surface; and it has generally been considered as consisting of

	By Measure.	By Weight.
Oxygen . . .	21	23
Nitrogen . . .	79	77
	<hr/> 100	<hr/> 100

Though these are what are usually termed the *essential* component parts of atmospheric air, it contains other substances, which to a certain

extent may be regarded as adventitious, and the quantity of which is liable to vary*: of these, *carbonic acid and aqueous vapour* are the most important and constant. The quantity of the former may usually be considered as amounting to less than about $\cdot 01$ per cent.† The presence of *aqueous vapour* in the atmosphere is shown in a variety of ways, but most easily by exposing to it certain deliquescent substances, which liquify or increase in weight in consequence of its absorption; and as the gases in general, unless artificially dried, also contain vapour of water, it is necessary, in delicate experiments, and in ascertaining their specific gravity, to take this ingredient into the account (see p. 443), or to separate it by proper means, such as exposure to very deliquescent substances, among which fused chloride of calcium is especially useful, under the precautions already mentioned.

The quantity of water contained in air and gases is subject to variation. From the experiments of Saussure, Dalton, and Ure, already referred to, it appears that 100 cubic inches of atmospheric air at 57° , are capable of retaining 0.35 grains of watery vapour; in this state the air may be considered at its maximum of humidity; it would also appear that all the gases take up the same quantity of water when under similar circumstances, and that it consequently depends, not upon the density or composition, but upon the bulk of the gaseous fluid; and from Dalton's researches, already mentioned, it may be concluded that the vapour forms an independent atmosphere, mixed, but not combined with the air. (See DANIELL'S *Meteorology*.)

Hygrosopes and hygrometers are instruments which show the presence of water in the air, its variation in quantity, and its actual quantity existing in a given bulk of air at any given time. Saussure employed a human hair, which, by its dilatations and contractions in moisture and dryness, turned an index; Deluc used a thin strip of whalebone in the same way; Wilson employs a rat's bladder, filled with mercury, and tied on to a large thermometer-tube; by its dilatation and contraction the mercury falls and rises in the tube, and thus indicates changes in the moisture of the air. Dr. Mason's hygrometer shows the relative

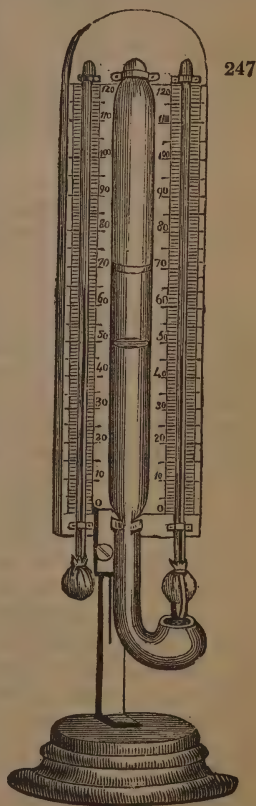
* Lavoisier's experiments gave 27 measures of oxygen and 73 nitrogen: Priestley stated the oxygen to vary from 20 to 25 *per cent.*: Cavendish estimated it at 20 *per cent.*: Berthollet found in the air of Cairo and of Paris 22 of oxygen: Saussure in Geneva 21 to 22: De Marty in Catalonia, in all situations, 21 to 22; Davy, at Bristol and upon the west coast of England, during westerly winds, 21. The same in air from the coast of Guinea. Berger on the Jura, and on the mountains and in the valleys of Savoy, 20.3 to 21.6: Configliachi on the Simplon 21, and in the Rice-fields of the Milanese 20.8: Gay Lussac, 22,000 feet above the surface, and in Paris, 21.49: Dalton in England 20.7 to 20.8: seldom 21; but on Jan. 8, 1825, Barom. 30.9 and wind north east, 21.15. Gay Lussac and Humboldt,

instead of 21, as in the external air, found 20.2 in the Théâtre François during the performance. (L. GMELIN, *Handbuch*, i. 443.)

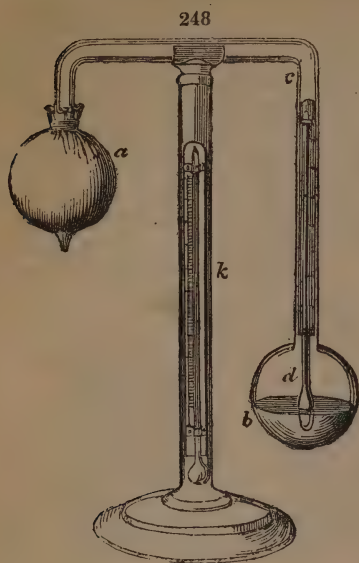
† Saussure and Gay Lussac found the usual proportion of carbonic acid in the air from the summit of Mont Blanc, and 650 toises above Paris. Beauvais found scarcely a trace of carbonic acid in the air over the sea off Dieppe, but the usual proportion inland. According to Saussure the proportion varies with the season: the air in a meadow, in August, contained 0.000713; in Jan., 0.000479; in Nov., in rainy and stormy weather, 0.000425. Dalton estimates the carbonic acid at 0.001; Configliachi the maximum at 0.008, and Humboldt (probably an excess) at 0.005 to 0.018. (L. GMELIN.)

dryness and moisture of the atmosphere by the degree of cold produced by evaporation from a given surface. If two delicate thermometers have their bulbs covered with a thin piece of muslin, and if the one be dry and the other moist, the depression of the latter will be directly as the rapidity or amount of evaporation, and this again will chiefly depend upon the state of the circumambient air as to moisture: if it be charged with vapour, no evaporation from the wet bulb will ensue, and consequently the mercury in that thermometer will remain stationary: if, on the contrary, it be very dry, it will eagerly abstract vapour from the humid surface, and a corresponding degree of cold will be indicated by the depression of the mercury in the humid thermometer, as compared with the standard or dry thermometer. The annexed wood-cut shows the arrangement of the thermometers in Dr. Mason's instrument. He covers the bulbs with white silk, and that intended for the hygrometric indications is kept constantly moist by the capillary action of a thread of floss silk which is attached to it, and of which one end dips into the cup of water forming the lower end of a reservoir, which acts upon the principle of the bird fountain. In this instrument the hygrometric degrees are best expressed by those of the thermometric scale.

Mr. Daniell's hygrometer shows the constituent temperature of the moisture in the atmosphere, by its precipitation upon a cold surface; comparing this with the temperature of the atmosphere, the difference furnishes a datum for calculating the quantity of vapour in a given quantity of air. A detailed account of this instrument, and of the observations made with it, is given by Mr. Daniell in the *Quarterly Journal of Science* (vols. viii. ix. and x.), and in his "Essays." It consists of a tube, twice bent at right angles, at the ends of which are two thin glass bulbs; the one tightly covered by a piece of fine muslin, the other about half full of ether, and including a very delicate thermometer, the small oblong bulb of which is immersed into the ether, as shown in fig. 248. The bulbs and tubes are filled with the vapour of ether, to the entire exclusion of air, so that when the instrument is placed as in the figure, and the bulb *a* is cooled by dropping a few drops of good ether upon it, (see page 183 in reference to the phenomena of evaporation, and the construction of the cryophorus, which acts upon the same principle,) the interior ethereal vapour is in part condensed, and the liquid in *b* furnishes a fresh portion, by which its temperature is more or less lowered, as shown by the immersed thermometer *d*. Now when the bulb *b* is thus cooled, it is in the condi-



tion of any other cold body, and has a tendency to cause the deposition



of aërial moisture upon its surface; and the temperature at which such deposition will take place, or in other words the *dew-point*, will vary with the hygrometric state of the air. In very humid atmospheres the thermometer *d* will scarcely have fallen a degree before a ring of moisture is evident upon *b*, coinciding with the surface of the included ether, and being the point of lowest temperature: in dry atmospheres, on the other hand, it will be necessary to reduce the temperature of the included thermometer, by the continuous evaporation of ether from the covered bulb, many degrees, before the ring of dew is visible. Now the temperature at which this ring of dew is deposited, or the *dew-point*, may be accurately read off upon the interior thermometer by observing the degree at which it stands, *at the*

moment of the first appearance of the ring of dew; and this observation may be corrected or verified by again observing the temperature or degree at which *the ring of dew vanishes*: these two observations seldom differ more than a degree or two, and the mean may be assumed as correct, for the errors, if any, must lie in opposite directions. There is a second or external thermometer attached to this instrument at *k*, which shows the temperature of the air at the time of making the observation; and the difference between the two thermometers at that time gives the exact temperature required for the deposition of the aërial moisture, or is the dew-point; the extent of this difference is as the dryness of the air, and may thus be used as an hygrometric term. On one day, for instance, the external thermometer being 60° , the internal fell to 48° before the ring of dew appeared: on another day the external thermometer stood at 66° , and the internal had only fallen to 64° when the dew-ring appeared; here therefore the degree of dryness might be called 12° in the former, and 2° in the latter case. It is obvious then, in regard to this instrument, that it furnishes a very ready and exact method for the determination of the *dew-point*.

“By means of the dew-point accurately ascertained,” Mr. Daniell observes, “many points of the utmost interest to chemical and meteorological science may be determined. By mere inspection of tables properly constructed, we can at once determine the elasticity and density of the aqueous vapour—its weight in a cubic foot of the air—the degree of dryness either upon the thermometric or the hygrometric scale—and the rate of evaporation; when the air is saturated, the precipitation is instantaneous, *i.e.*, the dew-point coincides with the temperature of the air.

In this country, the degree of dryness measured in thermometric degrees seldom reaches 30° , that is to say, the dew-point is seldom 30° below the temperature of the air, but in the Deccan, with a temperature of 90° , the dew-point has been seen as low as 29° , making the degree of dryness 61° .

"The more accurate mode, however, of expressing the moisture of the air from an observation of the temperature and dew-point, is by the quotient of the division of the elasticity of vapour at the real atmospheric temperature, by the elasticity at the temperature of the dew-point: for, calling the term of saturation 1000, as the elasticity of vapour at the temperature of the air is to the elasticity of vapour at the temperature of the dew-point, so is the term of saturation to the observed degree of moisture. Thus, with regard to the observation in the Deccan,

$$1.430 : 0.194 :: 1000 : 135.$$

"The fourth term is the degree of moisture on the hygrometric scale."

As an average of results, the ordinary constituents of the atmosphere appear to be in the following proportions:

	By Measure.	By Weight.
Nitrogen	77.5	75.55
Oxygen	21.	23.32
Aqueous vapour	1.42	1.03
Carbonic acid	0.08	0.10
	100	100

If the relative bulk of oxygen to nitrogen be considered as 1 to 4, and many analysts will not allow that the atmosphere contains more than 20 of oxygen to 80 of nitrogen, it follows that, in reference to the atomic theory, it is a mixture of one proportional of oxygen = 8, and two of nitrogen = $14 \times 2 = 28$; which may be thus represented:—

Oxygen. 8	=	Atmospheric Air.
Nitrogen. 14		
Nitrogen. 14		

In addition to the substances above enumerated as the *constant* component parts of our atmosphere, it contains, in certain situations, minute quantities of what may be termed *accidental ingredients*, the nature and proportions of which depend upon a variety of causes; and "as the sea contains a little of everything that is soluble in water, so," as Dr. Prout observes, "the atmosphere may be conceived to contain a little of everything that is capable of assuming the gaseous form." It has even been supposed that all substances may impart in this way portions of foreign matter, which, though infinitely small, would in time accumulate into sensible proportions; the formation of *aërolites* has even been referred to such a cause: but the fallacy of this hypothesis has been satisfactorily demonstrated by Faraday (*On the existence of a limit to vaporisation*, *Phil. Trans.*, 1826, p. 484), his argument being founded on the principle by which Dr. Wollaston accounted for the limited extent of the atmosphere (*Phil. Trans.*, 1822, p. 89); namely, that its boundary is dependent upon the opposing powers of elasticity and gravitation. On passing

upwards from the earth's surface the air becomes more and more attenuated in consequence of the gradually diminishing pressure of the superincumbent part, and its tension or elasticity is proportionately diminished: when the diminution is such that the elasticity is a force not more powerful than the attraction of gravity, then a limit to the atmosphere must occur: the particles of the atmosphere there tend to separate with a certain force, but this force is not greater than the attraction of gravity which tends to make them approach the earth and each other; and as expansion would necessarily give rise to diminished tension, the force of gravity would then be strongest, and consequently cause contraction, until the powers were balanced as before.

This condition of ærial particles, Mr. Faraday applies to all other vapours, and infers that every kind of matter ceases to assume the elastic form, when the gravitation of its particles exceeds the elasticity of its vapour; and by proving that a variety of substances, kept for some years in a confined space and with moisture, underwent no evaporation, he has furnished ample grounds for denying the existence of a miscellaneous collection of vapours in the atmosphere.

To revert, however, to the *extraneous matters*, as they may be called, which have actually been detected, or may fairly be presumed to exist at times in the air. We observe, in London, that traces of sulphurous and sulphuric acid are observable, and also of sulphate of ammonia, which salt we sometimes see upon dirty windows in small stellated spots: these, as well as finely-divided carbonaceous matter, are no doubt derived from coal-smoke. In the same way the air in the vicinity of certain manufactories, reducing-furnaces, and other places where large quantities of peculiar gases or vapours may be generated, will be liable to more or less *local contamination*. In the vicinity of the sea, and especially during storms, the rain which falls contains traces of salt, and during a thunder-storm it may possibly afford slight indications of nitric acid (p. 325). Sometimes rain and snow have been coloured by extraneous matters, mechanically diffused through the air; this has occasionally been traced to minute lichens, and other cryptogamous plants, brought from a distance by the winds, and diffused in myriads through the atmosphere; and sometimes to volcanic dust composed of earthy and metallic matters in a state of extreme comminution. The substances foreign to our atmosphere, and held in it in what may be termed a state of solution, are probably more numerous and various, though little understood, and from their nature, and the minute quantities in which they exist, very difficult of detection or examination. Various forms of *infection*, and *malaria* or *marsh-miasma*, are instances of such contaminations, and it is not improbable, from the manner in which they appear to be decomposed and destroyed by chlorine, that they consist of some hydrogenated compounds. Dr. Prout (*Bridgewater Treatise*, p. 350,) has suggested the possibility of some form of selenium being occasionally present in the air, so as to produce catarrhal epidemics, and in favour of the production of diseases by some such foreign matters, adduces the following observations which occurred to him during the presence of the epidemic cholera. "He had for some years been occupied in investigations regarding the atmosphere, and for more than six weeks previous to the appearance of

cholera in London, had almost every day been engaged in endeavouring to determine with the utmost possible accuracy the weight of a given quantity of air, under precisely the same circumstances of temperature and pressure. On a particular day, the 9th of February, 1832, the weight of the air suddenly appeared to rise above the usual standard. As the rise was at the time supposed to be the result of some accidental error, the succeeding observations were made with the most rigid scrutiny. On the days immediately following, the weight of the air still continued above the standard, and retained its augmented weight during the whole time the experiments were carried on, namely, about six weeks longer: the increase of weight was small, but still decided and real." Dr. Prout then goes on to state, that on the 9th of February the wind, which had been previously west, veered round to the east, and that precisely on the change of the wind, the first cases of the epidemic cholera were reported in London, and that from that time the disease continued to spread. I bring forward these observations not only as curious in themselves, but as showing, at least one cause of a possible discrepancy in the different estimates of the specific gravity of atmospheric air.

It has already been remarked, that in all common cases of combustion in atmospheric air, the oxygen enters into new combinations, whilst the nitrogen remains passive. In the same way, in the function of respiration, a portion of the oxygen is converted into carbonic acid, and is expired along with the unaltered nitrogen. This constant consumption of oxygen has induced theorists to seek for some method of its restitution in a pure state to the atmosphere; and Dr. Priestley suggested the functions of the vegetable creation as one source of such renovation. But it appears from the calculations of De Saussure, that in these inquiries the enormous bulk or quantity of the atmosphere has been forgotten, and that the united effect of the different deteriorating processes would not occasion any sensible difference in the chemical composition of the whole mass for many hundred years. In these speculations it must always be remembered that the different parts of the atmosphere are constantly kept in a uniform state of mixture, by the propensity which gaseous bodies have, notwithstanding material differences in their specific gravities, to diffuse themselves equably through each other, and that this equality of mixture is further promoted by the constant agitation to which the air is subjected by winds, and by the varied temperature of different portions of the earth's surface.

The combustion of substances in the air under ordinary circumstances will be explained, by reference to the details given in the chapter on Oxygen (p. 360). Some peculiar cases of combustion, however, which require more extended notice, have been ingeniously investigated by Sir H. Davy (*Essay on Flame*, and *Phil. Trans.*, 1817). In examining the effect of *rarefaction* upon combustion, he found that when hydrogen gas was inflamed at a fine orifice, so as to make a jet of flame of about one-sixth of an inch in height, and introduced under the receiver of an air-pump containing from 200 to 300 cubical inches of air, the flame enlarged as the receiver became exhausted; and when the gauge indicated a pressure between four and five times less than that of the atmosphere, was at its maximum of size; it then gradually diminished below, but

burned above, till the pressure was between seven and eight times less, when it became extinguished.

To ascertain whether the effect depended upon the deficiency of oxygen, he used a larger jet with the same apparatus, when the flame burned longer, and this when the atmosphere was rarefied ten times. When the larger jet was used, the point of the glass tube became white-hot, and continued red-hot till the flame was extinguished. It therefore occurred to him, that the heat communicated to the gas by this tube, was the cause that the combustion continued longer in the last trials when the larger flame was used; and the following experiments confirmed the conclusion. A piece of wire of platinum was coiled round the top of the tube, so as to reach into and above the flame. The jet of gas of one-sixth of an inch in height was lighted, and the exhaustion made; the wire of platinum soon became white-hot in the centre of the flame, and a small point of wire near the top fused; it continued white-hot till the pressure was six times less; when it was ten times less it continued red-hot at the upper part, and as long as it was dull red, the gas, though extinguished below, continued to burn in contact with the hot wire, and the combustion did not cease until the pressure was reduced thirteen times.

It appears from this result, that the flame of hydrogen is extinguished in rarefied atmospheres, only when the heat it produces is insufficient to keep up the combustion, which appears to be when it is incapable of communicating visible ignition to metal, and as this is the temperature required for the inflammation of hydrogen at common pressures, it appears that its *combustibility* is neither diminished nor increased by rarefaction from the removal of pressure.

According to this view with respect to hydrogen, it should follow that, amongst other combustible bodies, those which require least heat for their combustion ought to burn in more rarefied air than those that require more heat; and those that produce much heat in their combustion ought to burn, other circumstances being the same, in more rarefied air than those that produce little heat; and Sir Humphry's experiments confirm these conclusions. Thus, olefant gas, which approaches nearly to hydrogen in the heat produced by its combustion, and which does not require a much higher temperature for its inflammation, when its flame was made by a jet of gas from a bladder connected with a small tube furnished with a wire of platinum, under the same circumstances as hydrogen, ceased to burn when the pressure was diminished between ten and eleven times; and the flames of alcohol and of a wax-taper, which require a greater consumption of heat for the volatilization and decomposition of their combustible matter, were extinguished when the pressure was five or six times less without the wire of platinum, and seven or eight times less when the wire was kept in the flame. Light carburetted hydrogen, which produces less heat in combustion than any of the common combustible gases, except carbonic oxide, and which requires a higher temperature for its inflammation than any other, had its flame extinguished, even though the tube was furnished with the wire, when the pressure was below one-fourth.

The flame of carbonic oxide, which, though it produces little heat in

combustion, is as inflammable as hydrogen, burned when the wire was used, the pressure being one-sixth.

The flame of sulphuretted hydrogen, the heat of which is in some measure carried off by the sulphur produced by its decomposition during its combustion in rare air, when burned in the same apparatus as the olefiant and other gases, was extinguished when the pressure was one-seventh.

Sulphur, which requires a lower temperature for its combustion than any common inflammable substance, except phosphorus, burned with a very feeble blue flame in air rarefied fifteen times, and at this pressure the flame heated a wire of platinum to dull redness, nor was it extinguished till the pressure was reduced to one-twentieth*.

Phosphorus, as has been shown by M. Van Marum, burns in an atmosphere rarefied sixty times; and Sir Humphry found that phosphuretted hydrogen produced a flash of light when admitted into the best vacuum that could be made by an excellent pump of Nairn's construction.

The mixture of chlorine and hydrogen inflames at a much lower temperature than that of hydrogen and oxygen, and produces a considerable degree of heat in combustion: it was therefore probable that it would bear a greater degree of rarefaction, without having its power of exploding destroyed; and this was found by many trials to be actually the case, contrary to the assertion of M. de Grotthus. Oxygen and hydrogen, in the proportion to form water, will not explode by the electrical spark when rarefied eighteen times; but hydrogen and chlorine in the proportion to form hydrochloric acid gas, gave a distinct flash of light under the same circumstances, and they combined with visible inflammation when the spark was passed through them, the exhaustion being to one-twenty-fourth.

The experiment on the flame of hydrogen with the wire of platinum, and which holds good with the flames of the other gases, shows, that by preserving heat in rarefied air, or giving heat to a mixture, inflammation may be continued, when, under common circumstances, it would be extinguished. This was found to be the case in other instances, when the heat was differently communicated: thus, when camphor was burned in a glass tube, so as to make the upper part of the tube red-hot, the inflammation continued when the rarefaction was nine times, whereas it would only continue in air rarefied six times, when it was burned in a thick metallic tube which could not be considerably heated by it. (DAVY on *Flame*, p. 56.)

The influence of the admixture of other gases with atmospheric air upon its power of supporting combustion, is another subject which has been elucidated by Sir H. Davy's experiments. He found that a wax-

* The temperature of the atmosphere diminishes in a certain ratio with its height, which must be attended to in the conclusions respecting combustion in the upper regions of the atmosphere, and the elevation must be somewhat lower than in arithmetical progression, the pressure decreasing in geometrical progression. There is, however, every reason to believe that the taper would be extinguished at a height of between 9 and 10 miles, hydrogen between 12 and 13, and sulphur between 15 and 16.

taper was instantly extinguished in air mixed with one-tenth of silicated fluoric acid gas, and in air mixed with one sixth of hydrochloric acid gas; but the flame of hydrogen burned readily in those mixtures; and in mixtures in which the flame of hydrogen was extinguished the flame of sulphur burned.

The following simple experiment demonstrates this general principle. Into a long bottle with a narrow neck introduce a lighted taper, and let it burn till it is extinguished; carefully stop the bottle, and introduce another lighted taper; it will be extinguished before it reaches the bottom of the neck; then introduce a small tube containing zinc and diluted sulphuric acid, at the aperture of which the hydrogen is inflamed; the hydrogen will be found to burn in whatever part of the bottle the tube is placed: after the hydrogen is extinguished, introduce lighted sulphur; this will burn for some time; and after its extinction, phosphorus will be as luminous as in the air, and, if heated in the bottle, will produce a pale-yellow flame of considerable density.

In cases when the heat required for chemical union is very small, as in the instances of hydrogen and chlorine, a mixture which prevents inflammation will not prevent combination, *i. e.*, the gases will combine without any flash. Thus, in mixing two volumes of carburetted hydrogen with one of chlorine and hydrogen, hydrochloric acid was formed throughout the mixture, and heat produced, as was evident from the expansion when the spark passed, and the rapid contraction afterwards, but the heat was so quickly carried off by the quantity of carburetted hydrogen that no flash was visible.

Steam, and such vapours as require considerable heat for their formation, have a less power of preventing combustion than permanent gases. Sir H. Davy found that a very large quantity of steam was necessary to prevent sulphur from burning. Oxygen and hydrogen exploded by the electric spark, when mixed with five times their volume of steam; and even a mixture of air and carburetted hydrogen gas, the least explosive of all mixtures, required a third of steam to prevent its explosion; whereas one-fifth of nitrogen produced the effect. (DAVY on *Flame*, p. 87.)

In the course of the above experiments, Sir Humphry endeavoured to ascertain what would be the effect of condensation on flame in atmospheric air, and whether the cooling power of the nitrogen would increase in a lower ratio, as might be expected, than the heat produced by the increase of the quantity of matter entering into combustion. He found considerable difficulties in making the experiments with precision; but he ascertained that both the light and heat of the flames of the taper, of sulphur, and of hydrogen, were increased in air condensed four times, but not more than they would have been by an addition of one-fifth of oxygen.

He condensed air nearly five times, and ignited iron-wire to whiteness in it by the Voltaic apparatus, but the combustion took place with very little more brightness than in the common atmosphere, and would not continue as in oxygen; nor did charcoal burn much more brightly in this compressed air than in common air. These experiments show that (for certain limits at least), as rarefaction does not diminish considerably the

heat of flame in atmospheric air, so neither does condensation considerably increase it; a circumstance of great importance in the constitution of our atmosphere, which at all the heights or depths at which man can exist, still preserves the same relations to combustion.

§ VIII. SULPHUR.

SULPHUR, or *brimstone*, is a brittle substance, of a pale-yellow colour, somewhat translucent, insipid, and inodorous, but exhaling a peculiar odour when heated. The ancients used it in medicine, and its fumes were employed in bleaching wool. (PLINY, lib. xxxv. cap. xv.) Its specific gravity is 1.970, to 2.080. Its specific heat, as determined by Regnault, is 0.20259; by Dulong and Petit, 0.1880. It becomes negatively electrical by heat and by friction, and is a non-conductor of electricity*.

Sulphur is chiefly a mineral product, and occurs crystallized, its primitive form being an acute octoëdron with a rhombic base. These crystals are in a high degree doubly refractive. According to Mitscherlich, it has, when artificially crystallized, as when suffered gradually to cool after having been fused, a different primitive form, namely, an oblique rhombic prism. From its solutions in alcohol, ether, sulphuret of carbon, and chloride of sulphur, it is generally deposited in the octoëdral form. Crystals of native sulphur which have been formed by the condensation of sulphur vapour, as well as those which are deposited from a solution of sulphur in any menstruum, possess forms which are either identical, or connected by being referable to the same crystalline axes. Such, on the contrary, as are produced by the cooling of fused sulphur belong to a different system of crystallization. The condition determining the form is temperature: if the crystal be formed below 232° it belongs to the right prismatic system; if at that point, to the oblique prismatic. This is proved by the influence of temperature on a crystal of either system; a crystal of fusion, when first formed, is perfectly clear and transparent, but kept at common temperatures it soon becomes opaque, and presents the appearance of the roll-sulphur of commerce: the same change occurs when a native crystal is placed in a solution of salt which boils at 232° . The opacity is in both cases produced by a new arrangement of the particles of sulphur, by which, without any change in the exterior form, the internal structure of the crystal is altered to correspond to the crystallization peculiar to the temperature.

Native sulphur is principally brought to this country from Sicily, where it occurs in beds, in a blue clay formation, occupying the central half of

* Sulphur, in its ordinary state, always contains traces of hydrogen, which it gives off during the action of various bodies for which it has a powerful attraction. Thus, if equal weights of sulphur and copper, or iron-filings, be introduced into a retort, and heated, a portion of sulphuretted hydrogen is evolved at the period of their combination. When potassium and sulphur are heated together, a vivid combustion ensues, and a little sulphuretted hydrogen is evolved. Berzelius, by heating sulphur with oxide of lead, remarked the formation of water, but in such small and indefinite quantities, as induced him to adopt the generally received opinion, that the presence of hydrogen is accidental, and that it is not an element of sulphur.

the south coast of the island, and extending inwards as far as the district of Etna. This blue clay formation is considered by Dr. Daubeny of the same age with the gypsum bed of Paris, and therefore more recent than chalk. It contains beds of gypsum and of salt, and the sulphur is in some places associated with splendid crystals of sulphate of strontia. The supply of sulphur derived almost exclusively from Sicily is enormous: the average annual importation into England is between 16 and 17 thousand tons, at from 6*l.* to 10*l.* per ton. It undergoes a rough purification by fusion, and is brought into the market in square or oblong masses or blocks. At Bex, in Switzerland, sulphur occurs in the gypsum of the salt deposit; and it is found in the same rock in many other parts of Europe, generally in beds or masses; in Suabia, and near Schemnitz in Hungary, it is found in veins traversing granite and mica slate; and in the same rocks in Quito in Peru: near Gibraltar, it occurs in fetid limestone. Sulphur is also common in the fissures of lava near volcanic craters: there is a great deposit of this species of sulphur in the plain of the Solfatara near Naples. Sulphur is found abundantly combined with certain metals; the common ores of lead and copper are their *sulphurets*; sulphuret of iron, or *pyrites*, is also a very common mineral.

Sulphur is insoluble in water, and suffers no change by exposure to air. When it is heated to about 180°, it volatilizes, and its peculiar odour is strong and disagreeable; at about 216° it begins to fuse, and between 230° and 270°, it is perfectly liquid, and of a bright brownish-yellow colour; between 300° and 400° it becomes viscid, and of a deep brown colour, but regains its fluidity when cooled; at higher temperatures it again liquifies, and at about 600° it boils, and sublimates in the form of an orange-coloured vapour, and may be collected either in a solid or pulverulent state, according to the rapidity of the process and the size of the condensing vessels. The residue is the *sulphur vivum* of old pharmacy. When sulphur, which has been heated to about 300°, is poured into warm water, it acquires the consistency of soft wax, and hardens on cooling. In this state it is sometimes used to take impressions of gems and medals; it is of a reddish colour, and of the specific gravity 2·3. When slowly cooled after fusion, sulphur forms a fibrous crystalline mass; but Mr. Faraday has remarked that it sometimes retains its fluidity, and does not concrete till touched by some solid body. This state appears somewhat analogous to that of water cooled in a quiescent state below its freezing point. (*Quarterly Journal*, xxi. 392.) The following table shows the results of Dumas's experiments on the influence of temperature upon the colour and properties of sulphur:—

Temperature.		Hot Sulphur.	Sulphur suddenly cooled by immersion in water.
Fahr.	Cent.		
230°	110°	Very liquid: yellow	Very friable: usual colour
284	140	Liquid: deep yellow	Do. do.
338	170	Thick: orange yellow	Friable: do.
374	190	Thicker: orange	{ At first soft and transparent, then friable and opaque: usual colour
428	220	Viscid: reddish	
464 to 500	240 to 260	Very viscid: brown-red	Soft: transparent: amber colour
	Boiling pt.	Less viscid: brown-red	Very soft: transparent: reddish
			Do. do. brown-red.

In order that sulphur may retain its soft or viscid state it is not necessary, as sometimes directed, to keep it long in a fused state, but merely to take care that it has been raised to a due temperature and then suddenly cooled by dropping it into cold water; if poured into the water in mass, the interior cools slowly and reverts to its brittle state: here, therefore, the effect of what may be called *tempering* is the reverse of that produced upon steel, and somewhat corresponds with the phenomena presented by bronze.

Sulphur is commonly met with in three forms; namely, 1. *Massive* or native sulphur, already mentioned. 2. *Stick* or *roll* sulphur, which is chiefly obtained from sulphuret of copper in this country, and elsewhere abundantly from sulphuret of iron, or common pyrites; these ores are roasted, and the fumes received into a long chamber of brick-work, where the sulphur is gradually deposited; it is then purified by fusion, and cast into sticks. In this state, if grasped by the warm hand, it splits with a crackling noise. 3. *Sublimed* sulphur, or *flowers of sulphur*, which is in a pulverulent form, and procured by condensing the vapour of sulphur rapidly in capacious receivers; it is of a peculiar pale yellow colour, and when examined by a microscope appears composed of minute crystals; it is always somewhat sour, and therefore for certain pharmaceutical purposes is directed to be washed with hot water.

The sulphur of commerce occurs in three prevailing colours, namely, lemon yellow verging on green, dark yellow, and brown yellow; these shades result, partly at least, as the above table shows, from the different degrees of heat to which it has been exposed during its fusion or extraction on the great scale, the palest variety having been the least heated. The different modes of purifying sulphur are described by Dr. Ure in the first volume of the *Royal Inst. Journal*. (For a detailed account of the methods of obtaining and purifying sulphur, see also DUMAS: *Chimie appliquée aux Arts*.)

For some pharmaceutical purposes sulphur is precipitated from its alkaline solutions, by an acid, and, when washed and dried, is in the form of a yellowish-gray impalpable powder; this is the *milk of sulphur* and *precipitated sulphur* of the *Pharmacopœia*. Dr. Thomson considers it as a compound of sulphur and water. (*System of Chemistry*, vol. i. p. 285.)

The purity of sulphur may be judged of by heating it gradually upon a piece of platinum leaf; if free from earthy impurities, it should totally evaporate. It should also be perfectly soluble in boiling oil of turpentine. (AIKIN'S *Dictionary*, Art. SULPHUR.) According to Dr. Ure, sulphur is soluble in ten times its weight of boiling oil of turpentine at 316° forming a solution which remains clear at 180° . As it cools to the atmospheric temperature, crystalline needles form, which may be washed with cold alcohol or tepid water. The usual impurities of the sulphur, which are carbonate and sulphate of zinc, oxide and sulphuret of iron, sulphuret of arsenic, and silica, will remain unaffected by the volatile oil, and may be separately eliminated by the curious, though such separation is of little practical importance.

Sulphur dissolves with some difficulty, and in very small proportions, in alcohol; to effect this solution both substances should be brought together in the state of vapour. It is more soluble in sulphuric ether.

It appears from the statements of Dumas and of Mitscherlich that the density of sulphur vapour is about 6.6 (*Ann. de Chim. et Phys.*, L. 170, and LV. 5), so that supposing it to exist in the state of vapour at mean temperature and pressure, 100 cubic inches would weigh 206 grains, and its specific gravity to hydrogen would be as 96 to 1.

When heated in the atmosphere to a little above 300° , sulphur inflames and burns with a peculiar blue light; at a higher temperature its vapour kindles with a purple flame; and in oxygen it burns vividly, with a large lilac-coloured flame.

SULPHUR AND OXYGEN.—There are four definite compounds of sulphur and oxygen, all of which rank among the acids; namely, 1. Sulphurous acid; 2. Sulphuric acid; 3. Hyposulphurous acid; 4. Hyposulphuric acid.

SULPHUROUS ACID. ($S + 2O$), or \hat{S} , or SO_2 , or \ddot{S} . This acid was first examined by Stahl, who called it *phlogisticated sulphuric acid*. Scheele, in 1774, pointed out a method of obtaining it; and about the same time, Priestley procured it in the gaseous form, and ascertained its leading properties. Berthollet examined it in 1782, and 1789 (*Mem. Paris*, 1782, and *Ann. de Chim.*, ii. 54); and in 1797, Fourcroy and Vauquelin published a detailed series of experiments upon it. (*Ann. de Chim.*, xxiv. 229.) Some experiments on it were also published by Dr. Thomson in 1803. (*NICHOLSON'S Journal*, vi. 93.) Its atomic composition was first accurately investigated by Davy, by Gay Lussac, and by Berzelius.

At common temperatures and pressures sulphurous acid is a gaseous body, which may be obtained by several processes. It may be procured directly, by burning sulphur in oxygen gas; or indirectly, by boiling two parts of mercury in three of sulphuric acid; or by heating, in a retort, a mixture of equal parts of black oxide of manganese and sulphur. It must be collected and preserved over mercury; for water takes up rather more than thirty times its bulk of this gas. For all the common purposes of experiment it may be collected in dry stopper-bottles, as directed at page 366. It is often generated by the action of charcoal, wood, and various organic matters upon sulphuric acid, but in those cases it is mixed with carbonic acid. These processes generally resolve themselves into the deoxidizement of sulphuric acid, for when one atom of oxygen is abstracted from that acid, the remaining elements are left in the proportions constituting sulphurous acid.

The specific gravity of sulphurous acid gas is 2.22 (2.2105, TURNER), and 100 cubical inches weigh between 68 and 69 grains. (At 60° and 30 inches Bar., 68.691 grains. TURNER. At 32° , 72.8660 grains. THOMSON.) Its specific gravity compared with hydrogen is as 32 to 1.

Sulphurous acid is one of the most easily condensible of the gases. Monge and Clouet found, that at the freezing point, and under pressure, it assumed a liquid form; the experiments of Faraday place the pressure required for this purpose at two atmospheres. M. Bussy (*Ann. of Phil.*, viii. 307. N. S.) has shown that this acid may be obtained in the liquid form at common atmospheric pressure, by passing it through tubes surrounded by a freezing mixture of salt and snow. (FARADAY'S *Manipula-*

tion, p. 215.) In this state it is a limpid liquid of the sp. gr. of 1.45. It boils at 14° , and evaporates with such rapidity at common temperatures as to generate a great degree of cold; by its aid mercury may easily be frozen, and it produces cold enough to liquify chlorine, ammonia, and cyanogen. It conducts electricity (KEMP). When this liquid sulphurous acid is exposed in a humid state to cold, a crystalline solid is formed, containing about 20 per cent. of water (perhaps 1 equivalent of acid + 1 of water). A similar compound is often observed to invest the bubbles of gas produced by pouring the liquid acid into water.

When sulphur is burned in pure and perfectly dry oxygen, sulphurous acid is produced, without any change in the volume of the gas, so that its composition is learned by the increase of weight; and as 100 cubic inches of oxygen dissolve between 34 and 35 grains of sulphur, it is obvious that sulphurous acid is composed of equal weights of sulphur and oxygen; or of

								Berzelius.
Sulphur	1	..	16	..	50	.. 49.968
Oxygen	2	..	16	..	50	.. 50.032
<hr/>				<hr/>				<hr/>
Sulphurous acid			1		32		100	100.000

According to Mitscherlich's estimate of the specific gravity of sulphur vapour, sulphurous acid consists of 100 volumes of oxygen gas, and 16 of the vapour of sulphur, condensed into 100 volumes: or one volume of oxygen combined with one-sixth of a volume of sulphur vapour constitute one volume of sulphurous acid.

Sulphurous acid gas has a suffocating odour; it is fatal to animal life, and extinguishes most combustibles when immersed into it in an ignited state: hence it is sometimes resorted to for the purpose of extinguishing the burning soot in a chimney, as by throwing a handful of sulphur, in such a case, into the fire: it vividly maintains the combustion of potassium and sodium. At mean temperature and pressure, recently-boiled water takes up about 33 volumes (37, GRAHAM) of sulphurous acid gas; the solution has a sulphurous and somewhat astringent taste, and it bleaches many vegetable colours; but, by keeping, it acquires a sour flavour, and reddens the generality of vegetable blues. Upon some colouring matters, as that of cochineal, it has little action; and when it does destroy colour, the original tint may often be restored by a stronger acid. A red rose, for instance, is bleached by dipping into a solution of sulphurous acid; but the colour is restored by immersion in dilute sulphuric acid. According to Grotthus, the sulphurous acid and certain colouring matters combine into colourless compounds, which are decomposed by more powerful acids. A singular bleaching effect is produced upon some flowers by burning a little sulphur, so that the fumes of the sulphurous acid may come into contact with their petals: the dark-coloured dahlias, and heart's-ease, may thus be amusingly variegated. Obtained by burning sulphur, this acid is much used in bleaching cotton goods (*Quarterly Journ. of Science*, iv. 196), also for whitening silk and wool, and altering the colour of hops.

When the aqueous solution of sulphurous acid is boiled, the gas escapes, but not when it is frozen. Its specific gravity at 60° is 1.05.

Alcohol dissolves sulphurous acid more copiously than water; one volume taking up more than 100 of the gas.

Pure liquid sulphurous acid (that is, the condensed gas,) suffers no decomposition by the voltaic current, but when dissolved in water the solution yields oxygen at the anode, and hydrogen and sulphur at the cathode. A solution containing sulphuric acid in addition, is a better conductor: it gives very little gas at either electrode: that at the anode is oxygen, that at the cathode pure hydrogen, and from the cathode arises a white turbid stream consisting of diffused sulphur. "I conclude that the sulphurous acid was not affected by the electric current, and that the water only was electrically decomposed: that at the anode the oxygen from the water converted the sulphurous into sulphuric acid; and at the cathode, the hydrogen, electrically evolved, decomposed the sulphurous acid, combining with its oxygen, and setting the sulphur free: that the sulphur at the negative electrode was only a secondary result." (FARADAY, *Phil. Trans.*, 1834, p. 97.)

Sulphurous acid suffers no change at a red heat; but if mixed with hydrogen, and passed through a red-hot tube, water is formed and sulphur deposited; under the same circumstances, it is also decomposed by charcoal, by potassium, and sodium, and probably by several other metals. It undergoes no change when mixed with oxygen, unless humidity or water be present, in which case a portion of sulphuric acid is slowly formed. When mixed with chlorine, and in contact with water, sulphurous acid gives rise to sulphuric and hydrochloric acid, but the perfectly dry gases have no mutual action. So also iodine and bromine are without action on sulphurous acid unless water be present, when sulphuric acid, and hydriodic and hydrobromic acids are formed. The chloric, bromic, and iodic acids are decomposed by sulphurous acid, with the evolution of chlorine, bromine, and iodine, and the formation of sulphuric acid. When gaseous sulphurous acid is mixed with hydrochloric, hydriodic, or hydrobromic acid gases, they mutually decompose each other; water, and chloride, iodide and bromide of sulphur, are formed: but when these acids are in aqueous solution they then do not decompose each other. Peroxide of lead, or of manganese, added to the aqueous solution of sulphurous acid, convert it into sulphuric acid, and destroy its odour. With moist nitrous acid vapour, or with liquid nitrous acid, it forms a peculiar crystalline compound which will be referred to under the head *Sulphuric Acid*.

Vapour baths, in which sulphurous acid with or without steam is applied to the surface of the body, have of late years been much resorted to in the treatment of certain cutaneous complaints, and in rheumatic and other painful affections. The arrangements for this purpose employed in Paris are described and depicted by Dumas, (*Chimie App. aux Arts*: see also PEREIRA, *Elements of Materia Medica*.)

SULPHUROUS ACID AND AMMONIA. SULPHITE OF AMMONIA. ($S + 2O$) + $(n + 3h)$, or $\bar{S} + A$.—When sulphurous acid gas is passed into aqueous solution of ammonia, a sulphite of ammonia is formed, which may be obtained in prismatic crystals: exposed to air it absorbs oxygen, and passes into sulphate of ammonia: heated out of contact of air it yields

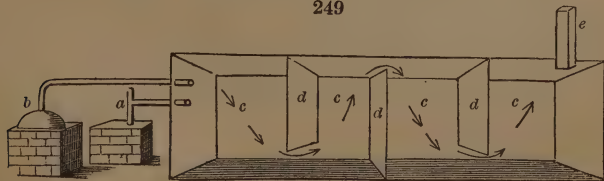
water, ammonia, and a sublimate of acid sulphite. Sulphite of ammonia is very soluble in water, and produces cold during its solution.

SULFIMIDE.—The mutual action of dry sulphurous acid and ammonia has been studied by Rose: when these gases, deprived of humidity, are combined, they produce deep yellow crystals, which contain the elements of 1 atom of ammonia and 1 atom of sulphurous acid: when there is great excess of sulphurous acid gas present, a compound in which equal volumes are condensed, and which therefore corresponds to a bisulphite of ammonia, is obtained; but no basic compound can be obtained by the employment of any excess of ammonia. The neutral compound has been chiefly examined by Rose; it is termed by Dumas, *Sulfimide*. (*Chim. App. aux Arts*, v. 709.)

Exposed to the air, sulfimide becomes white and deliquesces, and gradually passes into sulphate and hyposulphite of ammonia, and although to some tests it presents the characters of a sulphite of ammonia, with others, and especially with nitrate of silver, it acts as a hyposulphite. Dumas considers it as a hydrated amide, having the formula $(S + O) + (n + 2h) + (h + O)$: these elements are equivalent to those of an anhydrous sulphite of ammonia; or $(n + 3h) + (S + 2O)$.

SULPHURIC ACID. $(S + 3O)$ or S' , or SO_3 or \ddot{S} .—This important acid was formerly chiefly obtained by the distillation of sulphate of iron, or *green vitriol*, and was, therefore, termed *oil of vitriol*. It is now almost exclusively procured in this country by the combustion of a mixture of about eight parts of sulphur and one of nitre. The history of its discovery has already been adverted to (p. 20). The process of its manufacture is generally conducted nearly as follows: the mixture of sulphur and nitre is burned in a furnace, so placed that the resulting fumes may pass into a capacious leaden chamber (frequently 100 feet long, 20 to 30 feet wide, and 10 to 16 feet high), the floor of which is covered with water, and into which steam is also generally introduced: in many works several of these chambers, or *houses*, as they are termed, are ranged side by side in covered buildings. The following cut will serve to give some idea of the internal construction of one of these houses:—*a* is the furnace for the combustion of the sulphur and nitre, the fumes from which pass into the chamber and meet with the steam generated in the boiler *b*; the interior of the chamber is divided into several partitions, *c c*, by the diaphragms *d d*, which are alternately open at top and bottom, so that the vapours pass in the direction of the darts, and are exposed to a large

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condensing surface. *e* is a chimney or ventilator. The water which collects in the bottom of this chamber gradually becomes more and more

sour, and is, in fact, a diluted sulphuric acid; when it has thus acquired a certain specific gravity it is drawn off into shallow leaden boilers, or evaporators, where it is evaporated till it acquires the specific gravity of 1.70, at which density the acid would begin to act upon the lead, and the heat required for its further evaporation would endanger the softening of the metal; in that degree of concentration, therefore, the acid is run off into boilers, or rather into stills of platinum, which are set upon cast-iron, and in which the further boiling down of the acid is continued until it attains the specific gravity of 1.84; it is then drawn off by a syphon into a platinum cistern or cooler, and is thence transferred into *carbboys*, or large bottles protected by basket-work, each holding about 100 pounds of the acid. Before the introduction of platinum vessels for this purpose, the latter evaporation was performed in glass retorts, the lifting and emptying of which, when containing many pounds of the acid, was a very hazardous operation; the price of the acid fell, in consequence, from fourpence to about three-halfpence, or less, per pound. The manufacture of sulphuric acid is carried on upon a most extensive scale in Great Britain; the quantity annually produced, probably not falling far short of sixty thousand tons, or about one hundred million of pounds, which, at the estimated value of ten shillings per cwt., amounts to above 600,000*l*.

Although the acid obtained by the above process is commonly called *sulphuric acid* (or oil of vitriol) we shall soon find that it is in fact a definite combination of anhydrous sulphuric acid and water, composed of 1 atom anhydrous acid + 1 atom water, and sometimes therefore called a *protosulphate of water*.

In the above process, the theory of which will be presently explained, the sulphurous acid is in fact converted into sulphuric acid by the agency of nitric oxide and water. Several other methods of forming sulphuric acid have been suggested, but not hitherto applied on a large scale; among them the following deserves particular notice:—"When a mixture of sulphurous acid and air is made to pass over spongy platinum at a high temperature, the sulphurous acid is converted into sulphuric acid at the expense of the oxygen of the air. Mr. P. Phillips, who first made this observation, has founded upon it a method of preparing sulphuric acid on the large scale, which although not yet sufficiently tried to establish its advantage as a manufacturing process, is still of great interest in a scientific point of view, and deserves consideration. Sulphur is burned, or iron pyrites in place of it, and the sulphurous acid produced is mixed with an excess of air by a blowing apparatus, and carried through a tube filled with the platinum sponge, or balls of fine platinum wire. The vapours of sulphuric acid formed which are mixed with the nitrogen of the air are condensed in a long and narrow vessel of lead in an upright position, filled with pebbles which are kept constantly wet by a small stream of water admitted at the top, and which percolates downwards." (GRAHAM.)

It has long been an object with the manufacturer to obtain sulphuric acid without the aid of nitre, and a patent has been obtained for a process of this kind by Mr. Hill. It consists in submitting coarsely-powdered iron-pyrites (bisulphuret of iron) to a red heat, in cylinders communi-

eating with a leaden chamber containing water; part of the sulphur, as it burns out of the pyrites, appears at once to pass into the state of sulphuric acid; with the help of nitre the pyrites might perhaps be more economically employed.

The great consumers of sulphuric acid are the manufacturers of soda from common salt, and of chlorine or chloride of lime for the use of bleachers; there are also many chemical products dependent upon it, such as citric, tartaric, nitric, and hydrochloric acids; sulphate of soda; and sulphate of magnesia; and others of less note; it is also in constant demand by dyers, calico-printers, bleachers of various materials, the manufacturers of blacking, of soda-water, of various pigments, and by the refiners of gold and silver, and the purifiers of oil and tallow.

Sulphuric acid, as it usually occurs, is a limpid, inodorous, colourless fluid, of an oily consistence, and of the specific gravity of about 1·84. Dr. Ure observes that he has frequently boiled the pure acid till only one-half remained in the retort; yet at the temperature of 60° Fahrenheit, has never found the specific gravity of acid, so concentrated, to exceed 1·8455. The number 1·850, which has been assigned for the density of pure oil of vitriol, is erroneous, and ought to be corrected. Genuine commercial acid should never surpass 1·8455; when it is denser, we may infer sophistication, or negligence, in the manufacture.

Sulphuric acid boils at a temperature of about 620°, which, therefore, approaches a red heat, and distils over without decomposition. The density of its vapour was found by Mitscherlich to be 3. The calculated density is 2·762. Its boiling-point diminishes with its dilution; when of the specific gravity of 1·78 it boils at 435°; and at 350°, when its specific gravity is 1·65. (DALTON, *Chem. Phil.*, ii. 404.) In illustration of its fixedness at all common temperatures, Bellani placed a piece of zinc foil in the upper part of a closed bottle, the bottom of which was covered with the concentrated acid: the metal retained its bright surface at the end of two years. The concentrated acid freezes at -15°; and at the same time contracts considerably in its dimensions: acid of the specific gravity of 1·78 (which is a definite hydrate) containing 1 atom of anhydrous sulphuric acid and 2 atoms of water, on the contrary, freezes at +40°, but if the density be either increased or diminished, a greater cold is required for its congelation. (MACNAB, *Phil. Trans.*, vol. LXXvii., and KEIR, *Phil. Trans.*, vol. LXXviii.)

Sulphuric acid is intensely acid and caustic; it acts speedily upon the cuticle, occasioning a biting sensation, and a soapy feel of the part: its taste, even when very largely diluted, is extremely sour, and it powerfully reddens litmus. It has a strong attraction for water, so that when exposed for a short time to air, it absorbs aqueous vapour from the atmosphere and increases rapidly in bulk; in moist weather three parts increase to four in the course of 24 hours, and by longer exposure, a much larger quantity of water is taken up, so that the acid requires to be preserved in well-stopped vessels. It is this property which renders it applicable to the drying of certain gases, and to the purposes of evaporation and desiccation under the exhausted receiver of the air-pump; and hence the cold produced in the experiment described at p. 184. When sulphuric acid is suddenly mixed with water, mutual condensation ensues, much

heat, therefore, is evolved (p. 164). Four parts of acid and one of water produce, when thus mixed, a temperature $= 300^{\circ}$. According to Dr. Ure, the greatest heat is evolved by mixing 73 of acid with 27 of water. Even a boiling temperature does not prevent sulphuric acid taking up moisture from the air: hence it cannot be concentrated so well in an open as in a close vessel; on which account retorts of glass, or platinum-stills are used for the last stage of its concentration by the manufacturers. The mixture of sulphuric acid with ice or snow causes its immediate liquifaction, and as this liquifaction, consistently with the theory of latent heat, produces cold, while on the other hand the union of the acid with the water evolves heat, the resulting temperature of such mixture, depends upon the relative proportions of the substances mixed. Four parts of acid and one of snow, or pounded ice, evolve heat; but four parts of snow and one of acid generate cold.

Sulphuric acid possesses intense chemical powers; it displaces the greater number of other acids from their combinations; and, probably in consequence of its strong affinity for water, it chars most animal and vegetable substances, and acquires a brown tinge from the smallest particles of straw, cement, or even dust, that accidentally fall into it: it appears capable of dissolving small portions of charcoal, and also of sulphur, tellurium, and selenium; these substances give it various tints of brown, red, and green, or blue, and are precipitated when the acid is diluted with water; but if heat be applied they are oxidized at the expense of the acid, and sulphurous acid is evolved.

When heated with charcoal, sulphuric acid gives rise to the production of carbonic and sulphurous acids; with phosphorus it produces phosphoric and sulphurous acids; and, with sulphur, sulphurous acid is the only product. It is decomposed by several of the metals, which become oxidized, and evolve sulphurous acid, as shown in the production of this acid, by boiling sulphuric acid with mercury, tin, lead, &c. When metals are dissolved in *diluted* sulphuric acid, the water only is decomposed, and its oxygen, being transferred to the metal, forms a *metallic oxide*, which unites to the sulphuric acid to form a *sulphate*, whilst the hydrogen is evolved in the gaseous form.

It appears from Mr. Faraday's experiments (*Phil. Trans.*, 1834, p. 82), that sulphuric acid is not electrolysable, and that the anhydrous acid is not a conductor. The appearance of sulphur, when the common acid is subjected to the action of a powerful battery, at the negative pole, is referable to a secondary action (p. 314). But the electrolysis of hydrated sulphuric acid, and more especially of some of the sulphates, involves many interesting points respecting the ultimate constitution of those bodies, which we shall again refer to when considering the *salts of the metals*. (DANIELL, *Phil. Trans.*, 1839, p. 89; 1840, p. 209.)

The presence of sulphuric acid, either free or in any soluble combination, is detected by solution of baryta: if, for instance, a solution of chloride of barium be added to any liquid containing sulphuric acid or a sulphate, a white precipitate falls, which is *sulphate of baryta*, and is characterized by its insolubility in acids and alkalis. 117 parts of dry sulphate of baryta are equivalent to 40 of dry sulphuric acid. The

soluble salts of lead are also delicate tests of the presence of sulphuric acid: they indicate it by a white precipitate, insoluble in nitric acid.

In consequence of the great consumption of sulphuric acid, it is highly important to the consumer to be able to judge of its value and purity: the *specific gravity* may generally be depended upon as indicative of its strength, and we have several valuable tables showing the quantity of real or dry sulphuric acid contained in the liquid or diluted acid of various specific gravities.

Mr. Dalton (*New System of Chemical Philosophy*, vol. ii. p. 404) has published a table, exhibiting the specific gravity and boiling-point of the acid, of various strengths. Dr. Ure has also given several tables relating to this subject, in his *Experiments to determine the Law of Progression followed in the Density of Sulphuric Acid at different Degrees of Dilution*. (*Quarterly Journal of Science and the Arts*, vol. iv. p. 114.) See, also, URE'S *Dictionary*, Art. ACID (SULPHURIC). An extremely useful table of this kind will also be found in PARKES' *Essays* (vol. ii. p. 444).

The following is Dr. Ure's table:—

Liq.	Sp. Gr.	Dry.	Liq.	Sp. Gr.	Dry.	Liq.	Sp. Gr.	Dry.
100	1·8485	81·54	66	1·5503	53·82	32	1·2334	26·09
99	1·8475	80·72	65	1·5390	53·00	31	1·2260	25·28
98	1·8460	79·90	64	1·5280	52·18	30	1·2184	24·46
97	1·8439	79·09	63	1·5170	51·37	29	1·2108	23·65
96	1·8410	78·28	62	1·5066	50·55	28	1·2032	22·83
95	1·8376	77·46	61	1·4960	49·74	27	1·1956	22·01
94	1·8336	76·65	60	1·4860	48·92	26	1·1876	21·20
93	1·8290	75·83	59	1·4760	48·11	25	1·1792	20·38
92	1·8233	75·02	58	1·4660	47·29	24	1·1706	19·57
91	1·8179	74·20	57	1·4560	46·48	23	1·1626	18·75
90	1·8115	73·39	56	1·4460	45·66	22	1·1549	17·94
89	1·8043	72·57	55	1·4360	44·85	21	1·1480	17·12
88	1·7962	71·75	54	1·4265	44·03	20	1·1410	16·31
87	1·7870	70·94	53	1·4170	43·22	19	1·1330	15·49
86	1·7774	70·12	52	1·4073	42·40	18	1·1246	14·68
85	1·7673	69·31	51	1·3977	41·58	17	1·1165	13·86
84	1·7570	68·49	50	1·3884	40·77	16	1·1090	13·05
83	1·7465	67·68	49	1·3788	39·95	15	1·1019	12·23
82	1·7360	66·86	48	1·3697	39·14	14	1·0953	11·41
81	1·7245	66·05	47	1·3612	38·32	13	1·0887	10·60
80	1·7100	65·23	46	1·3530	37·51	12	1·0809	9·78
79	1·6993	64·42	45	1·3440	36·69	11	1·0743	8·97
78	1·6870	63·60	44	1·3345	35·88	10	1·0682	8·15
77	1·6750	62·78	43	1·3255	35·06	9	1·0614	7·34
76	1·6630	61·97	42	1·3165	34·25	8	1·0544	6·52
75	1·6520	61·15	41	1·3080	33·43	7	1·0477	5·71
74	1·6415	60·34	40	1·2999	32·61	6	1·0405	4·89
73	1·6321	59·52	39	1·2913	31·80	5	1·0336	4·08
72	1·6204	58·71	38	1·2826	30·98	4	1·0268	3·26
71	1·6090	57·89	37	1·2740	30·17	3	1·0206	2·446
70	1·5975	57·08	36	1·2654	29·35	2	1·0140	1·63
69	1·5868	56·26	35	1·2572	28·54	1	1·0074	0·8154
68	1·5760	55·45	34	1·2490	27·72			
67	1·5648	54·63	33	1·2409	26·91			

In ascertaining the specific gravity of sulphuric acid, the *temperature* requires minute attention, because from the small specific heat of the acid it is easily affected, and because it greatly influences the density. On removing the thermometer from the acid, it speedily rises in the air to 75° or 80° , though the temperature of the apartment be only 60° ; afterwards it slowly falls to 60° . If this thermometer, having its bulb covered with a film of dilute acid (from absorbing atmospheric moisture), be plunged into a strong acid, it will rise 10° or more, and an elevation equal to 10° diminishes the density of oil of vitriol by 0.005; 1000 parts being heated from 60° to 212° , become 1043 in volume, and the sp. gr. which was 1.848, falls to 1.772, being the number corresponding to a dilution of 14 per cent. of water.

But it is also necessary to ascertain that the sulphuric acid under examination leaves no residue on evaporation. If the acid of commerce contain dissolved sulphate of lead, it becomes turbid on dilution, so that its remaining clear when mixed with water is some proof of its purity, as far at least as lead is concerned. The simplest mode of judging of the purity of this acid is to introduce a given weight into a platinum capsule and evaporate it; if it leaves more than one *per cent.* of solid residue, it has probably been intentionally sophisticated. It often holds sulphate of potassa in solution, 2.5 per cent. of which increases the specific gravity of the concentrated acid to 1.860; hence the necessity, where accuracy is required, of determining the value of the acid by its *saturating power*. For this purpose, a given weight of the acid is diluted with six or eight parts of water, and pure anhydrous carbonate of soda added until the solution is exactly neutral (see *Alcalimetry*). Every 54 parts of such carbonate of soda required for this purpose, are equivalent to 40 parts of the anhydrous acid, or to 49 of the liquid sulphuric acid, or oil of vitriol, of the specific gravity of 1.84.

For some purposes of delicate chemical research, it is necessary to purify the acid by distillation, and this operation requires much precaution, when conducted in a glass retort, in consequence of the violent jerks which the production of its vapour occasions, and which often break the vessel; this may be prevented by putting some strips of platinum into the acid; it then boils quietly, and it is only necessary to take care that the neck of the retort and receiver are not broken in consequence of the high temperature of the condensing acid. This very useful contrivance to the practical chemist was shown me many years ago by Sir James South.

Dr. Ure has the following remarks on the distillation of this acid:—
 “I take a plain glass retort, capable of holding from two to four quarts of water, and put into it about a pint measure of the sulphuric acid, (and a few fragments of glass,) connecting the retort with a large globular receiver, by means of a glass tube four feet long, and from one to two inches in diameter. The tube fits very loosely at both ends. The retort is placed over a charcoal fire, and the flame is made to play gently on its bottom. When the acid begins to boil smartly, sudden explosions of dense vapour rush forth from time to time, which would infallibly break small vessels. Here, however, these expansions are safely permitted, by the large capacity of the retort and receiver, as well as by

the easy communication with the air at both ends of the adopter tube. Should the retort, indeed, be exposed to a great intensity of flame, the vapour will no doubt be generated with incoercible rapidity, and break the apparatus. But this accident can proceed only from gross imprudence. It resembles, in suddenness, the explosion of gunpowder, and illustrates admirably Dr. Black's observation, that, but for the great latent heat of steam, a mass of water, powerfully heated, would explode on reaching the boiling temperature. I have ascertained, that the specific caloric of the vapour of sulphuric acid is very small, and hence the danger to which rash operators may be exposed during its distillation. Hence, also, it is unnecessary to surround the receiver with cold water, as when alcohol and most other liquids are distilled. Indeed the application of cold to the bottom of the receiver generally causes it, in the present operation, to crack. By the above method, I have made the concentrated oil of vitriol flow over in a continuous slender stream, without the globe becoming sensibly hot."

Cases of poisoning by sulphuric acid are not unfrequent; the best antidotes are copious draughts of chalk and water, and of carbonate of magnesia and water. (ORFILA.)

NATIVE SULPHURIC ACID has been found by Professor Baldassari, in the cavities of a small volcanic hill, called Zoccolino, near Sienna.

ANHYDROUS SULPHURIC ACID.—When sulphuric acid was procured by the distillation of green vitriol, it was frequently observed that a portion concreted into a white mass of radiated crystals. The same substance has also been remarked as occasionally formed in the acid of the English manufacturers. It has been called *glacial* or *fuming sulphuric acid*, and is considered as the pure, or *anhydrous acid*. When crystallized green vitriol, or protosulphate of iron, is exposed to a dull red heat, it crumbles down into a white powder, and loses the greater part of its water of crystallization. (See *Sulphate of Iron*.) In this state it is put into a coated earthen or green glass retort, and gradually exposed to an intense red or even white heat; a dark-coloured acid liquor distils over, of a specific gravity of about 1.89, which has been called *Nordhausen*, or *German sulphuric acid*, which smokes when exposed to air, from the escape of the highly volatile *dry* sulphuric acid, which is united in the brown liquid with a portion of hydrated acid. This brown, fuming acid, is in request as a ready and perfect solvent of indigo. When it is kept at a temperature below 32°, crystals form in it, which according to Mitscherlich are a definite compound of 2 atoms of anhydrous acid and 1 atom of water; it is resolved by heat into the common and the anhydrous acid.

The dry or *anhydrous sulphuric acid* may be separated from the brown or Nordhausen acid, by careful distillation from a retort into a dry and cold receiver; it passes over in drops, which concrete, on cooling, into a tenacious crystalline mass. This acid is liquid at a temperature above 66°; and at 78° its specific gravity, according to Bussy, is 1.97. (*Journal de Pharmacie*, x. 368.) When it has once congealed it is difficult to fuse it, because the first portions heated become vapour, and propel the rest forward; by slight pressure, however, this may be prevented. When kept in a temperature between 75° and 80° it gradually liquifies. At a

temperature somewhat above this, which, however, has not been accurately determined, it passes into the state of colourless vapour. In the absence of all moisture, it has no action upon litmus paper. It dissolves sulphur, forming brown, green, or blue compounds, according to the quantity taken up; when water is added, the sulphur is deposited. It also dissolves iodine, forming with it a blue-green solution. Passed through a red-hot porcelain tube, anhydrous sulphuric acid is resolved into *one volume of oxygen and two of sulphurous acid*. Caustic lime or baryta heated in its vapour, become ignited, and converted into sulphates. The attraction of this anhydrous acid for water is such as to produce intense heat, and a hissing noise, when small portions of it are thrown into that fluid; and if a sufficient quantity of it be added to such a proportion of water as is required to convert it into hydrated acid, they combine with heat, light, and explosion.

The liquid acid, from sulphate of iron, yields about one-fourth its weight of anhydrous acid by distillation; but if this cannot be procured, the anhydrous acid may be obtained, according to Berzelius, by the distillation of such other sulphates as easily part with their acid: those sulphates which require a very elevated temperature, are less fit for the purpose, because the acid is then apt to be resolved into sulphurous acid and oxygen. Bisulphate of soda, or persulphate of iron, may thus be employed. The former may be made by mixing in a crucible three parts of thoroughly-desiccated sulphate of soda with two of common sulphuric acid, and heating them till the ebullition occasioned by the escape of water has ceased. The resulting mass is then to be pulverized, transferred to a porcelain retort, and distilled at a red heat; the acid which passes over may be collected in a receiver cooled by ice: it is generally of a dark colour, which appears to arise from dust accidentally present. A persulphate of iron, applicable to the same purpose, may be procured by mixing finely-powdered peroxide of iron into a thin paste with common sulphuric acid, and gradually heating it (below redness) till they combine into a saline mass, which is to be powdered and subjected to distillation as before. The acid thus obtained generally contains a little water, and if it crystallizes, it forms brittle foliaceous crystals. Carefully distilled by a gentle heat, the anhydrous acid passes over, and common liquid acid (hydrated) remains in the retort.

It appears, then, that this extraordinary substance, which is thus volatile and easy of congelation, forms, by combining with water, the fixed and difficultly-congealable liquid which we commonly term *sulphuric acid*, or *oil of vitriol*, and that it contains sulphur and oxygen in the same proportions as they exist in the dry sulphates. From its resolution when passed through a red-hot tube, into one volume of sulphurous acid and half a volume of oxygen, and likewise from the experiments of Berzelius upon the direct acidification of sulphur, it appears that *anhydrous sulphuric acid* consists of

					Berzelius.			
Sulphur	.	.	1	.	16	.	40	40.14
Oxygen	.	.	3	.	24	.	60	59.86
<hr/>				<hr/>				
Anhydrous Sulphuric Acid	1				40		100	100.00

And the liquid, hydrous, or common sulphuric acid consists of

				Davy and Dalton.
Dry sulphuric acid	1	40	81.63	81
Water	1	9	18.37	19
Hydrate of Sulphuric Acid	1	49	100.00	100

The compound of sulphuric acid and water of the specific gravity 1.78, which has been above alluded to as congealing at 40° remains solid till raised to 45° , and is a definite combination of 1 atom of anhydrous acid + 2 atoms of water; and lastly, the acid of specific gravity 1.632 appears also to be a definite hydrate containing 1 atom of anhydrous acid and 3 atoms of water, for it is to this strength that a dilute sulphuric acid evaporated in vacuo at 212° is reduced, and it is also in these proportions that sulphuric acid and water suffer the greatest diminution of bulk in combining. It would appear, therefore, that there are four definite hydrates of sulphuric acid; of which the following are the formulæ, and their abbreviations:—

	Formulæ.	Abbreviations
Anhydrous Acid	$(S + 3O)$	S'
Hydrate in the Nordhausen Acid	$2(S + 3O) + (h + o)$	$2S' + q$
Oil of Vitriol, sp. gr. 1.845	$(S + 3O) + (h + o)$	$S' + q$
Acid of sp. gr. 1.780	$(S + 3O) + 2(h + o)$	$S' + 2q$
Acid of sp. gr. 1.632	$(S + 3O) + 3(h + o)$	$S' + 3q$

Mr. Graham, in reference to the composition of the *sulphates*, arranges these formulæ as follows:—

Hydrate in the Nordhausen Acid	$(q + 2S')$	or	$HO, 2SO_3$
Oil of Vitriol	$(q + S')$		HO, SO_3
Acid of sp. gr. 1.780	$(q + S') + q'$		$HO, SO_3 + HO.$
Acid of sp. gr. 1.632	$(q + S') + 2q$		$HO, SO_3 + 2HO.$

THEORY OF THE PRODUCTION OF SULPHURIC ACID.—Having stated the properties and composition of anhydrous, and common sulphuric acid, we may now revert to the *theory of its formation* in the process of the combustion of sulphur and nitre. It was first supposed that the nitre merely yielded oxygen directly to the sulphur and so effected its perfect acidification; but the small quantity of nitre required, and the production of sulphurous and not sulphuric acid, when sulphur is either burned alone in pure oxygen gas, or when it is heated with peroxide of manganese and other substances which readily impart oxygen, seemed to indicate some other power possessed by the nitre; that this is the case was proved by Clément and Désormes (*Ann. de Chim.*, lix.), and by Davy (*Elements of Chem. Philos.*, 276), to whom we owe the following explanation of the phenomena.

The sulphur by burning in contact with atmospheric air forms *sulphurous acid*; the nitre is at the same time decomposed, and yields *nitrous acid*. When these vapours (*i. e.*, sulphurous and nitrous acids) are perfectly dry, they do not act upon each other, but moisture being present in small quantity, they form a white solid, which is instantly decomposed by the contact of water; the nitrous acid reverts to the state of nitric oxide,

having transferred one additional proportional of oxygen to the sulphurous acid, and, with water, producing the sulphuric acid; while the nitric oxide, by the action of the air, again affords nitrous acid, which plays the same part as before.

Sulphurous acid consists of

16	Oxygen. 8	}	$16+16=32$
	8		

And nitrous acid contains

14	Oxygen. 8	}	$32+14=46$
	8		
	8		
	8		

Hence every *two* proportionals of sulphurous acid require *one* of nitrous acid, which transfers *two* of oxygen, and passes back into the state of nitric oxide, sulphuric acid being, at the same time, produced.

The gases, therefore, before decomposition, may be thus represented:—

Sulphur.	
16	Oxygen. 8
	8
Sulphur.	8
16	8
	8
Two proportionals of Sulphurous Acid.	

Nitrogen.	Oxygen. 8
14	8
	8
	8
One proportional of Nitrous Acid.	

And after decomposition as follows:—

Sulphur.					
16	Oxygen. 8	}	24		
	8				
Sulphur.	8	}	24		
	8				
16	Oxygen. 8	}	24		
	8				
	8				
Two proportionals of Sulphuric Acid.					
Nitrogen.					
14	Oxygen. 8	}	16		
	8				
One proportional of Nitric Oxide.					

Or the changes may be thus represented more briefly in symbols; namely two proportionals of *sulphurous acid*, and one of *nitrous acid*, $2(S + 2O)$

$+(n + 4O)$, become two proportionals of *sulphuric acid*, and one of *nitric oxide*, $2(S + 3O) + (n + 2O)$.

When liquid hyponitrous acid is mixed with sulphuric acid, a crystallized compound of the two acids is formed, provided the temperature be not too high, which, when put into water, evolves nitric oxide gas, and is, according to Gay Lussac, analogous to the above-mentioned substance produced by mixing humid sulphurous and nitrous acid gases. (*Ann. de Chim. et Phys.*, i. 408.)

SULPHURIC ACID AND AMMONIA. SULPHATE OF AMMONIA. GLAUBER'S SECRET SAL-AMMONIAC. SULPHATE OF OXIDE OF AMMONIUM.—This salt may be obtained directly by pouring a few drops of sulphuric acid into a bottle of gaseous ammonia; the ammonia is rapidly absorbed, and the salt crystallizes on the sides of the jar. It is usually prepared by saturating dilute sulphuric acid with *carbonate of ammonia*, or by decomposing hydrochlorate of ammonia by sulphuric acid. It is important as a source of *hydrochlorate of ammonia*, which is obtained by sublimation from a mixture of chloride of sodium and sulphate of ammonia; by this process sulphate of soda is also formed. (See *Sodium*.) For these purposes the *ammoniacal liquor* of gas-works, produced during the destructive distillation of coal, and the impure carbonates of ammonia formed by the distillation of bones and other refuse animal matters, are saturated by sulphuric acid, and the resulting sulphate of ammonia purified by crystallization.

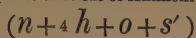
Sulphate of ammonia, in its driest state, includes one proportional of water. In its common form of six-sided prismatic crystals, it contains, according to Berzelius, two proportionals of water, being composed of

				Berzelius.
Ammonia	1	17	22.7	22.6
Sulphuric acid	1	40	53.3	53.1
Water	2	18	24.0	24.3
<hr/>				
Crystallized sulphate } of ammonia . . . }	1	75	100.0	100.0

It is soluble in two parts of water at 60° and in one at 212° . Its taste is bitter and pungent. When heated, it melts and in part sublimes, ammonia is given off, and a *bi-sulphate* remains containing 2 proportionals of acid + 1 of ammonia: at a higher temperature, nitrogen and water are given out, and sulphite of ammonia (or probably sulfimide) is formed.

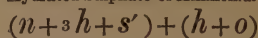
To assimilate the composition of this salt with the other sulphates, it is assumed to be a *sulphate of oxide of ammonium*; it cannot exist without the atom of water belonging to the sulphuric acid, and is not formed, as we shall presently find, by the mutual action of ammonia and anhydrous sulphuric acid: upon this (hypothetical) view therefore of its constitution, ammonia becomes converted into ammonium by uniting to the hydrogen of the water in the acid, and the oxygen of this water converts the ammonium ($n + 4h$) into oxide of ammonium ($n + 4h$) + O , and this, combined with the anhydrous sulphuric acid forms a sulphate of oxide of ammonium: it is evident that the elements of this hypothetical anhydrous sulphate of oxide of ammonium are equivalent to those of the hydrated sulphate of ammonia; for

Sulphate of Oxide of Ammonium.



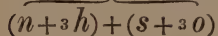
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Hydrated Sulphate of Ammonia.



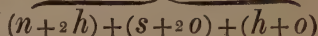
ANHYDROUS SULPHURIC ACID AND AMMONIA. SULFAMIDE. —The principal evidence in favour of the above view of the constitution of the sulphate of ammonia is derived from *the action of anhydrous sulphuric acid on ammonia*. By conducting dry gaseous ammonia into a glass vessel coated with a thin film of anhydrous sulphuric acid, Rose obtained a crystallized compound, differing in form from sulphate of ammonia, and in which neither sulphuric acid nor ammonia are evident to the usual tests, although their elements must manifestly be included in the compound: it seems probable, therefore, that it may be an *amide* (a hydrated sulfamide) for the elements

Anhydrous Sulphate of Ammonia.



=

Sulfamide and Water.



But the electrolytic decomposition of a solution of sulphate of ammonia, the phenomena of which have been described by Daniell (*Phil. Trans.*, 1839, p. 111), furnishes another view of the constitution of this and other sulphates, which on many accounts is extremely interesting and important in its theoretical bearings. Mr. Daniell found that hydrated sulphate of ammonia $= (n+3h)+(s+3o)+(h+o)$ is resolved by electrolysis into 1 equivalent of sulphur and 4 of oxygen, given off at the anelectrode, and into 1 equivalent of nitrogen and 4 equivalents of hydrogen, given off at the cathelectrode; so that its electrolytic formula would be $(n+4h)+(s+4o)$; thus representing it, not as a sulphate of oxide of ammonium, but as a compound of ammonium $(n+4h)$ with a peculiar anion composed of 1 equivalent of sulphur and 4 of oxygen $(s+4o)$. Such an anion Mr. Daniell provisionally designates *oxysulphion*; and hence, the common sulphate of ammonia he terms *oxysulphion of ammonium*.

NATIVE SULPHATE OF AMMONIA is sometimes found in volcanic products; it occurs in stalactitic concretions of a whitish or yellowish colour, and covered with a white efflorescence: it has thus been procured from fissures in the earth surrounding certain small lakes in Tuscany, near Sienna; and among the products of Etna and Vesuvius; it has been termed by Karsten, *Mascagnine*, from the name of its discoverer.

HYPOSULPHUROUS ACID. $(2s+2o)$ or $\underline{s'}$ or SO_2+s . —The existence of an acid compound of sulphur and oxygen, containing *one* atom of sulphur and *one* of oxygen ($16+8=24$), was first inferred by Dr. Thomson, in 1817, and the salts containing such a combination were originally described by Gay Lussac (*Ann. de Chim.*, lxxxv.), under the name of *sulphuretted sulphites*. Higgins (*Comparative View*, p. 49) and Berthollet had previously found that iron and zinc might be dissolved in aqueous sulphurous acid, without any evolution of hydrogen gas, and that they formed peculiar colourless crystallizable salts, which, acted upon by certain other acids, evolved sulphurous acid and sulphur. By exposing sulphuret of sodium in solution to the air, Vauquelin obtained an analogous compound of soda. Thomson first suggested the existence of a peculiar acid composed of sulphur with a minimum of oxygen, in these

compounds, in 1817 (*Syst. of Chem.*), and they were afterwards examined with much precision and ability by Herschel. (*Edin. Phil. Jour.*, i.) This acid has not been examined in a separate state, though Berzelius has suggested the probability of its existence in some of those peculiar coloured compounds of anhydrous sulphuric acid and sulphur, which have been above adverted to. When we attempt to decompose its compounds in the humid way, sulphurous acid escapes, and sulphur is precipitated. By adding slight excess of sulphuric acid to a dilute solution of hyposulphite of strontia, Sir John Herschel succeeded in separating the acid, but it very soon began to undergo spontaneous decomposition, and was immediately resolved into sulphurous acid and sulphur by heat.

Hyposulphurous acid is formed when *sulphites* are digested in close vessels with sulphur; or when solutions of the sulphurets of the alkaline bases are exposed to the air till they become colourless: it is also produced by the action of zinc or iron-filings upon the solution of sulphurous acid in water, and from these salts it may be transferred to several other bases. In the first case, the oxygen of the sulphurous acid divides itself between the original and the newly-added sulphur. In the latter, the zinc or iron combines with half the oxygen of the sulphurous acid; and the other half, remaining in combination with the sulphur, forms the new acid.

It has been shown by Rose (POGGENDORFF's *Annalen*, xxi.), that although the ratio of the sulphur to the oxygen, in this acid, is as 16 to 8, its *equivalent*, or combining proportion, is not 24, but 48, hence it must be considered as a compound of

Sulphur	.	.	.	2	.	32	.	66.67	} = {	Sulphur	.	.	.	1	.	16	.	33.33
Oxygen	.	.	.	2	.	16	.	33.33		Sulphurous acid	1	.	.	.	1	.	32	.
<hr/>										<hr/>								
Hyposulphurous acid				1		48		100.00						1		48		100.00

The *hyposulphites* are mostly soluble and of a bitter taste: the solutions of the alkaline hyposulphites occasion black precipitates in the nitrates of silver and mercury, which are *sulphurets*: the hyposulphites of lead and of baryta are thrown down in the form of white insoluble powders: the neutral hyposulphites dissolve recently-precipitated chloride of silver, and form with it a compound of a very sweet taste.

HYPOSULPHURIC ACID ($2S + 5O$) or S' or S_2O_5 , was discovered in 1819 by Gay Lussac and Welther. It was accidentally formed in an attempt to analyze oxide of manganese by the employment of sulphurous acid, when a peculiar salt was formed, which did not precipitate baryta. This salt was afterwards found to contain a distinct acid of sulphur, to which Gay Lussac gave the above name. (*Ann. de Chim. et Phys.*, x.) It is obtained by passing a current of sulphurous acid through a cold mixture of finely-powdered and pure peroxide of manganese and water. A solution is obtained, which is filtered and thoroughly agitated and digested with hydrated baryta, which must be added in small excess. The sulphuric acid and the greater part of the oxide of manganese are thus precipitated. The solution is again filtered and evaporated till it crystallizes, and the crystals of *hyposulphate of baryta* are a second time dissolved and obtained by evaporation, in order to procure them free from

manganese; they are then dried, powdered, weighed, and dissolved in water; and to every hundred parts of the dissolved salt, 18·78 parts of sulphuric acid, of the specific gravity of 1·84, diluted with four parts of water, are added. The baryta is thus thrown down in the state of sulphate, and the new acid remains in solution. Having been filtered, it is to be concentrated by exposure under the exhausted receiver of the air-pump, including a vessel of sulphuric acid, till it acquires the density of 1·347. If its exposure and evaporation be continued beyond this point, it is resolved into sulphuric and sulphurous acids. A temperature of 212° effects the same change in its composition. It is inodorous, sour, and reddens vegetable blues. It has not been obtained in an anhydrous state.

Neither oxygen, nor chlorine, nor nitric acid, nor peroxide of manganese, affect the composition of hyposulphuric acid at common temperatures; it dissolves zinc with the evolution of hydrogen, and hyposulphate of zinc results. It saturates the salifiable bases; and with lime, baryta, strontia, and protoxide of lead, it forms *soluble* compounds; whereas those formed by these bases with the sulphuric acid, are difficultly soluble or insoluble. Its salts, however, are not permanent at high temperatures, but when heated they are resolved into sulphates, with the escape of sulphurous acid; notwithstanding this, they remain *neutral*, though the quantity of sulphurous acid which escapes is such as would itself have saturated the base. The elements of this acid are in the relative proportions of 1 atom of sulphur and 2·5 oxygen, but its equivalent is not 36, but 72, hence it is constituted of

Sulphur 2 32 44·44	}	{	Sulphurous acid 1 32 44·44
Oxygen 5 40 55·56			Sulphuric acid 1 40 55·56
<hr/>			<hr/>
Hyposulphuric acid 1 72 100·00			1 72 100·00

SULPHUR AND CHLORINE. CHLORIDE OF SULPHUR. (*S + C*) or *S Cl*.—This compound was first described by Dr. Thomson, in 1804 (*NICHOLSON'S Journal*, vol. viii.); and afterwards more fully examined by Berthollet, junior. (*Mém. d'Arcueil*, t. i.) The chlorides of sulphur have also been examined by Rose (*POGGEND. Ann.*, xxi., 431), and by Dumas (*Ann. de Chim. et Phys.*, xlix. 205). When sulphur is heated in excess of dry chlorine, it absorbs rather more than twice its weight of that gas. Ten grains of sulphur absorb 30 cubic inches of chlorine, and produce a liquid of a greenish-yellow, by transmitted light, but orange-red by reflected light. (*DAVY, Elements*, p. 280.) The combination also takes place at common temperatures, and may be effected by passing excess of chlorine through a tube containing powdered sulphur. Chloride of sulphur exhales suffocating and irritating fumes when exposed to the air. Its specific gravity is 1·6: it is volatile below 200°. It boils at 280°, yielding vapour of the density of 4·70. It does not affect dry vegetable blues; but when water is present, it instantly reddens them, sulphur is deposited, and sulphurous, sulphuric, and hydrochloric acids are formed, in consequence of a decomposition of the water. It dissolves sulphur and phosphorus, and decomposes ammonia, according to Grouvelle, but according to Thomson it combines with ammonia, forming a purple or yellow compound. It also decomposes alcohol and ether: it is decomposed by

mercury, heat being evolved, sulphur deposited, and chloride of mercury formed. A fragment of potassium dropped into it presently burns and explodes. It absorbs phosgene gas. According to Davy, although this compound readily dissolves sulphur, it is incapable of absorbing chlorine. From the analysis of Davy and Dumas it consists of

Sulphur	. .	1	. .	16	. .	Dumas.
Chlorine	. .	1	. .	36	. .	31.4
<hr/>						68.6
Chloride of Sulphur		1		52		100.0

DICHLORIDE OF SULPHUR. BISULPHURET OF CHLORINE. SUBCHLORIDE OF SULPHUR ($2S + Cl$) or S_2Cl .—When the preceding liquid is saturated with sulphur, it deposits a portion, often in crystals, but retains, according to Bucholz, one additional proportional of sulphur, forming a yellow-brown liquid of the specific gravity of 1.700 and possessed of the general properties of the preceding. I have obtained beautiful tetraëdral crystals of sulphur from this liquid, and their deposition is remarkably influenced by light; it appears gradually to deposit the whole of its excess of sulphur. According to Rose (POGGENDORFF, *Ann.*, xxi.) this is the only chloride of sulphur, and the preceding compound analyzed by Davy and Dumas is a solution of chlorine in the dichloride. It consists of

Sulphur	. .	2	. .	32	. .	Rose.
Chlorine	. .	1	. .	36	. .	47.06
<hr/>						52.94
Dichloride of Sulphur		1		68		100.

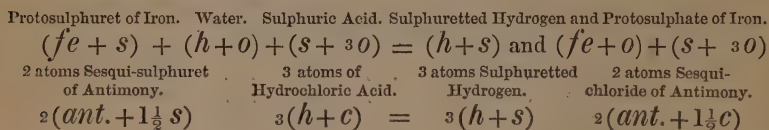
SULPHUR AND IODINE. IODIDE OF SULPHUR. ($S + i$).—Sulphur and iodine readily unite by a gentle heat, and form a black crystallizable compound, first described by Gay Lussac. (*Ann. de Chim.*, xci.) It is decomposed by a degree of heat a little exceeding that required for its formation, and, when boiled in water, the iodine goes off with the steam, and sulphur remains. It is probably a compound of one proportional of each of its components.

SULPHUR AND BROMINE. BROMIDE OF SULPHUR. ($S + b$).—When bromine is digested with sulphur, a red liquid compound results, which emits fumes when exposed to air, and has little action upon dry litmus paper, but powerfully reddens it when moist. It dissolves both bromine and sulphur. It is slowly acted on by cold water, but at 212° the action is violent, sulphuretted hydrogen is evolved, and hydrobromic and sulphuric acids are formed. Chlorine decomposes the bromide of sulphur, and chloride of sulphur is formed, with the evolution of bromine. The composition of this bromide has not been determined.

SULPHUR AND FLUORINE.—Davy obtained a fuming liquid, *Fluoride of Sulphur*, by distilling a mixture of sulphur and fluoride of lead.

SULPHUR AND HYDROGEN. SULPHURETTED HYDROGEN GAS. HYDROTHIONIC ACID. HYDROSULPHURIC ACID. SULPHYDRIC ACID. ($h + s$) or hs' , or HS .—This compound of sulphur and hydrogen was discovered by Scheele in 1777. When sulphur is heated or sublimed in hydrogen gas,

or when the gas is passed through melted sulphur, a small portion of sulphuretted hydrogen is slowly formed, but the action is very imperfect. The gas is readily obtained when sulphur is presented to *nascent* hydrogen, which is the case when proto-sulphuret of iron is acted upon by dilute sulphuric acid, or when one part of bruised sulphuret of antimony is heated with four of hydrochloric acid; or one part of pulverized sulphur and two of iron-filings may be made into a thin paste with water, and heated in a flask till the mixture blackens, after which, the addition of sulphuric acid diluted with four times its bulk of water, causes an abundant evolution of sulphuretted hydrogen. (*Ann. de Chim. et Phys.*, vii. 314.) In the case of the evolution of sulphuretted hydrogen by the action of sulphuric acid and water upon the proto-sulphuret of iron, water is decomposed, its hydrogen combines with the sulphur of the sulphuret to form sulphuretted hydrogen, and its oxygen converts the iron into protoxide, which, combining with the sulphuric acid, forms proto-sulphate of iron. When sesqui-sulphuret of antimony and hydrochloric acid are employed, sesqui-chloride of antimony is formed, and the hydrogen of the acid unites to the sulphur of the sulphuret to form sulphuretted hydrogen. These reactions are expressed in the following equations :



Dumas recommends sulphuret of calcium, or the double sulphuret of sodium, and iron obtained by fusing powdered pyrites with half its weight of dry carbonate of soda at a red heat, as sources of sulphuretted hydrogen when its rapid evolution is required; these sulphurets are to be acted on by hydrochloric acid.

Sulphuretted hydrogen is gaseous at common temperatures and pressures. Under a pressure of about 17 atmospheres at 50°, it assumes the liquid form: it is then limpid, and apparently possessed of a refractive power exceeding that of water; its specific gravity is about 0.9. It does not congeal when cooled down to 0. When a tube containing it was opened under water, it instantly and violently rushed forth under the form of gas. (FARADAY, *Phil. Trans.*, 1823, p. 92.)

Sulphuretted hydrogen gas may be collected over water, though, by agitation, that fluid absorbs nearly thrice its bulk. It has a peculiarly nauseous fetid odour, resembling that of rotten eggs, and so diffusible that a single cubic inch escaping into the atmosphere of a large room, is soon everywhere perceptible by its smell. 100 cubic inches weigh between 36 and 37 grains. Its specific gravity compared with air is as 1.17 to 1; and compared with hydrogen, as 17 to 1. According to Thomson its specific gravity is 1.1805; and 100 cubic inches, reduced to the temperature of 32°, weigh 38.6196 grains. Dumas gives its specific gravity as = 1.1912. It is inflammable, and during its slow combustion, sulphur is deposited, and water and sulphurous acid formed. It extinguishes the flame of a taper. When respired, it proves fatal; and it is very deleterious, even though largely diluted with atmospheric air. According to

the statement of Dupuytren and Thenard, a small bird died immediately in air containing only one 1500th of sulphuretted hydrogen; one 800th killed a middle-sized dog; and a horse perished in an atmosphere containing one 150th. Nausea, vertigo, headach, and a peculiar faintness, are common consequences when an atmosphere even slightly contaminated by sulphuretted hydrogen is breathed for any length of time, and as its escape in the laboratory cannot always be prevented, its effects may be counteracted by the diffusion of a little chlorine, or by sprinkling the room with an aqueous solution of chlorine. It exists in some mineral waters, and is found in foul sewers and in putrid eggs.

The aqueous solution of sulphuretted hydrogen is transparent and colourless when recently prepared, but it gradually becomes opalescent, and if exposed to air it deposits sulphur, and the greater part of the gas escapes. The whole of the gas is evolved by heat. It is an exceedingly delicate test of the presence of most of the metals, with which it forms coloured precipitates. One measure of sulphuretted hydrogen mixed with 20000 measures of hydrogen, carburetted hydrogen, or atmospheric air, produces a sensible discoloration of white lead or of oxide of bismuth, mixed with water, and spread upon a piece of card. In this way we may ascertain the presence, in coal-gas, of extremely small quantities of sulphuretted hydrogen; and may even form an estimate of its proportion, when too minute to be otherwise measured, by comparing the shade of colour with a series prepared for the purpose, by exposing slips of card covered with white lead and water to mixtures of sulphuretted hydrogen and common air, in known proportions. (HENRY, *Elements of Chemistry*.)

Sulphuretted hydrogen slightly reddens infusion of litmus, and moist litmus paper; it is generally classed among the hydracids, and does not, therefore, unite directly with the basic oxides, a metallic sulphuret and water being, as it is presumed, the result of their mutual reaction; it combines with certain sulphurets (basic sulphurets) and forms a class of *sulphur salts*; compounds, according to Graham, strictly analogous to the hydrated oxides, if we substitute sulphur for oxygen.

When one volume of sulphuretted hydrogen is detonated with half a volume of oxygen, water is formed and sulphur precipitated; the whole of the mixed gases being condensed: but when a volume of sulphuretted hydrogen, and a volume and a half of oxygen are inflamed in a detonating tube, one volume of sulphurous acid is produced, and water is formed. Thus the sulphur is transferred to one volume of the oxygen, and the hydrogen to the half volume. Sulphuretted hydrogen may also be decomposed by the Voltaic flame, in the apparatus shown in fig. 219, or by a succession of electric sparks. Its volume is unchanged, but the sulphur is thrown down. This gas, therefore, consists of

	Berzelius.				Vols.	100 C.I.
Sulphur	1	. 16	. 94.1	. 94.176	. 0.16	. 34.3
Hydrogen	1	. 1	. 5.9	. 5.824	. 1.00	. 2.1
Sulphuretted Hydrogen 1	17	100.0	100.000	100.000	1.00	36.4

Spongy platinum does not effect the combustion of a mixture of sulphuretted hydrogen and oxygen unless free hydrogen be also present.

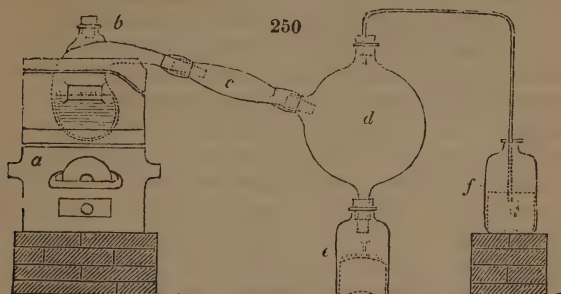
Chlorine, iodine, and bromine, instantly decompose sulphuretted hydrogen; when they are not in excess sulphur is deposited, and hydrochloric, hydriodic, and hydrobromic acids are formed. Nitric acid poured into the gas occasions a deposition of sulphur, and nitrous acid and water are formed, with considerable elevation of temperature, and occasionally flame. The aqueous solution of the gas is also decomposed by these reagents. Hence the method of preparing hydriodic and hydrobromic acids by passing sulphuretted hydrogen through water in which iodine or bromine is diffused, as already noticed. When sulphuretted hydrogen is mixed with its volume of nitric oxide over mercury, a diminution of bulk ensues, in consequence of the production of water; sulphur is deposited, and nitrous oxide remains in the vessel. When *two* volumes of sulphuretted hydrogen are mixed in an exhausted balloon with *one* of sulphurous acid, they mutually decompose each other, occasioning the production of water, and the deposition of sulphur; if the gases be perfectly dry, the action is slow. According to Thomson, the deposited matter is not sulphur, but a compound of sulphur, oxygen, and hydrogen, which he calls *hydrosulphurous acid*. (*Ann. of Phil.*, xii. 441.) Sulphuric acid also decomposes sulphuretted hydrogen; the results are water, sulphurous acid, and sulphur.

When potassium or sodium are heated in sulphuretted hydrogen, sulphurets of those metals are formed with vivid combustion, and pure hydrogen is liberated. When tin or lead are fused in the gas, they also decompose it, and absorb the sulphur, leaving a volume of hydrogen equal to that of the original gas. Passed over metallic oxides, water and metallic sulphurets are the results. The different oxides effect this decomposition at very different temperatures.

SULPHURETTED HYDROGEN AND AMMONIA. HYDROSULPHURET OF AMMONIA. HYDROSULPHATE OF AMMONIA. SULPHURET OF AMMONIUM. BOYLE'S FUMING LIQUOR. BEGUIN'S SULPHURETTED SPIRIT. $\frac{(s+h)}{(n+3h)}$, or $(hs' + A)$.—When ammonia and sulphuretted hydrogen gas are mixed, white fumes at first appear, which become yellow, and a yellow crystallized compound results. If this be obtained by the condensation of 1 volume of sulphuretted hydrogen and 2 of ammonia, it may be considered as consisting of 1 proportional of each of its components. The best way of combining the gases is to suffer them, previously dried, to pass by separate tubes to the bottom of a flask or bottle immersed in ice; the access of air should be prevented, and the escape of any uncondensed gas provided for by a safety-tube: the crystals thus produced are extremely volatile and deliquescent. When a current of sulphuretted hydrogen gas is passed through an aqueous solution of ammonia, a solution of hydrosulphate of ammonia is also formed.

A compound of sulphuretted hydrogen and ammonia, with excess of sulphur, and holding ammonia in solution, is obtained by distilling a mixture of about four parts of slaked quicklime, two of hydrochlorate of ammonia, and one of sulphur. The following is the disposition of the apparatus for this experiment: (see fig. 250) *a* is a small furnace; *b*, a tubulated earthen retort containing the above materials; *c*, an adapting tube; *d*, a glass balloon for condensing the vapour; *e*, a receiver; *f*, a bottle of water, into which the glass tube, issuing from the upper part of the balloon *d*,

is made to dip about half an inch. The product in the receiver *e*, may be mixed with the water in *f*, and the whole used for washing out the balloon *d*. In its concentrated state, this compound exhales white fumes, and was formerly called *Boyle's fuming liquor*. It is a deep-yellow liquid, smelling like a mixture of sulphuretted hydrogen and



ammonia. When kept in common white glass vessels, it renders them brown or black, in consequence of its action on the oxide of lead which the glass contains. It readily dissolves sulphur. According to Gay Lussac, no ammonia is decomposed in the above operation, but the sulphuretted hydrogen is formed by the union of sulphur with the hydrogen of the hydrochloric acid: the residue in the retort, consisting of sulphate of lime and chloride and sulphuret of calcium, is formed by the union of sulphur with part of the oxygen of the lime to produce sulphate of lime, the evolved calcium being divided between the chlorine and sulphur. Hydrosulphate of ammonia is occasionally used as a test or re-agent. It has been used medicinally as an emetic; and in the dose of from 5 to 8 drops, in the treatment of diabetes.

The neutral hydrosulphate of ammonia resulting from the condensation of 2 volumes of ammonia by 1 volume of sulphuretted hydrogen is a compound of

Ammonia	1	17	50
Sulphuretted hydrogen : :	1	17	50
<hr/>	<hr/>	<hr/>	<hr/>
Hydrosulphate of ammonia	1	34	100

The elements, therefore, which constitute this salt are $(n + 3h) + (s + h)$, and these, upon the ammonium theory, are equivalent to $(n + 4h) + s$, which represents it as a *sulphuret of ammonium*.

BISULPHURET OF HYDROGEN. SUPERSULPHURETTED HYDROGEN. $(h + 2s)$, or HS_2 .—This is a yellow liquid, first described by Berthollet, (*Ann. de Chim.*, xxv.,) formed by dropping a strong solution of bisulphuret of potassium into dilute hydrochloric acid (see *Sulphurets of Potassium*). If the acid be dropped into the sulphuretted solution, sulphuretted hydrogen escapes, and sulphur is precipitated; but proceeding as above directed, the greater part of the sulphur remains united to the hydrogen, and a peculiar yellow liquid is the result. The success of the

experiment depends much upon the state of concentration of the alkaline solution, which should neither be too strong nor too dilute, and should be slightly warm, and stirred during the mixture.

Bisulphuret of hydrogen may also be obtained by boiling equal parts of lime and flowers of sulphur, in five or six parts of water, for about half an hour; when cold, the supernatant brown liquor (containing hydro-sulphuret of lime, with excess of sulphur) is to be poured off, and gradually added to hydrochloric acid, either of its usual strength, or diluted with its bulk of water, taking care to have excess of acid, and to stir the mixture after each addition. Under these circumstances some sulphur is precipitated, and the sulphuretted hydrogen is not evolved, but unites to an additional proportion of sulphur to form the bisulphuret, which gradually subsides in the form of a yellow viscid fluid, which may be kept for some days in the acid liquor, or in dilute hydrochloric acid. Its specific gravity is about 1.7. It is often involved in a coating of sulphur, from which it may be squeezed out by gentle pressure with a glass rod. In water it is slowly resolved into sulphur and sulphuretted hydrogen, and more rapidly by alkaline solutions. At 212° it is rapidly decomposed. Oxide of gold or silver is immediately reduced by it with slight explosion and incandescence. Other substances, such as silica, and the alkaline earths, decompose it, without themselves suffering change; in this, and its property of bleaching, Thenard (*Ann. de Chim. et Phys.*, xlviii. 79,) suggests an analogy between it and peroxide of hydrogen. It has sometimes been regarded as an acid, and hence termed *hydropersulphuric acid*: its elements are

Sulphur	2 . .	32 . .	97
Hydrogen	1 . .	1 . .	3
<hr/>			
Bisulphuret of hydrogen	1	33	100

SULPHUR AND NITROGEN do not form any definite compound, though the nitrogen evolved during the decomposition of certain animal substances often seems to contain sulphur. It is possible also, that the purple compound obtained by the action of ammonia on chloride of sulphur, may contain a sulphuret of nitrogen.

§ IX. PHOSPHORUS.

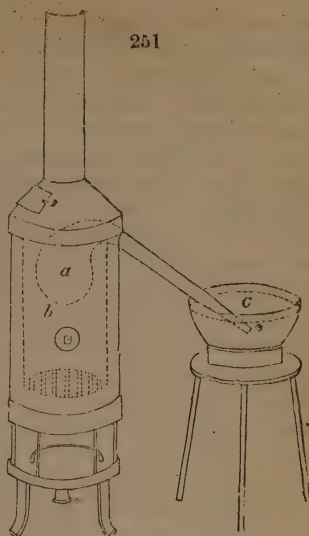
THIS remarkable substance was discovered in 1669 by Brandt, a merchant of Hamburg; he obtained it whilst attempting to extract from human urine a liquid capable of converting silver into gold. (HOMBERG, *Mém. Par.*, x. 84.) Kunckel, an eminent German chemist, aware of the source whence it was obtained, imparted the secret to Kraft of Dresden, who repaired to Hamburg to learn the details of the process, for which he paid Brandt two hundred dollars; but in the mean time Kunckel prepared and exhibited it, and was therefore considered as one of its discoverers. In 1680 an account of it was published in the *Phil. Trans.*, and it became known under the name of *English Phosphorus*, in consequence of the large quantities of it prepared in London, under the

direction of the celebrated Boyle, by his assistant, Godfrey Hankwitz*. In 1737 the process for its preparation was sold by a stranger to the French government, an account of which was published by Hellot, (*Mém. de l'Acad.*, 1737.) It was tedious and disgusting: from five (muids) hogsheads of urine 38 pounds of residue were obtained by evaporation, and this, by four distillations, yielded at most 4 ounces of phosphorus. The process was improved by Margraff, Gahn, and Scheele, and afterwards by Fourcroy and Vauquelin.

Phosphorus, so termed from its property of shining in the dark, (from *φωσ* light, and *φερεειν* to bear,) may be obtained on the small scale, by distilling phosphoric acid, previously fused with one-fourth its weight of powdered charcoal, at a red heat. This mixture is pulverized and put into the coated green-glass or stoneware retort *a* (fig. 251), placed in the furnace *b*; the tube of the retort should be immersed about half an inch into the basin of water, *c*. A great quantity of gas escapes, some of which is spontaneously inflammable, and when the retort has obtained a bright red heat, a substance looking like wax, of a reddish colour, begins to pass over. This, which is impure phosphorus, may be rendered pure by melting it under warm water, and squeezing it through a piece of fine shamoy leather; but great care must be taken that none adheres to the nails or fingers, as it would inflame on taking them out of the water, and produce a painful and troublesome burn. In performing this distillation, a high temperature is required, so that the furnace should be sufficiently capacious to hold a body of charcoal piled up above the retort, which, especially if of earthenware, (which becomes permeable to the vapour of phosphorus, at a red heat,) must be coated with a mixture of slaked lime and solution of borax; this mixture may be laid on with a brush, in two or three successive coats, and forms an excellent *nitrifiable lute*.

Phosphorus may also be obtained by adding solution of nitrate of lead or nitrate of mercury to urine, collecting, washing, and drying the precipitate, and distilling it, as above, with a fourth its weight of powdered charcoal. These precipitates are impure phosphates of lead and mercury; the latter is the easiest of decomposition.

Upon the large scale, phosphorus is most economically obtained from



* The founder of the Chemical Establishment, long known as "Godfrey's," in Southampton Street, Covent Garden. I have a print of this Chemist, by Veretue, which, it is said, he presented to his

customers on taking leave of them to sell phosphorus abroad: he is surrounded with the apparatus used in preparing it. Boyle described the process in a little work, entitled *Aërial Noctiluca*.

the impure superphosphate of lime, procured by acting upon powdered *bone earth* by sulphuric acid. The following is the mode of proceeding:

On twenty pounds of calcined bone, finely powdered, pour twenty quarts of water, and eight pounds of sulphuric acid, diluted with an equal weight of water. Let these materials be stirred together, and simmered for about six hours. Let the whole be then put into a conical bag of linen to separate the clear liquor, and wash the residuum till the water ceases to taste acid. Evaporate the strained liquor, and when reduced to about half its bulk, let it cool. A white sediment will form, which must be allowed to subside; the clear solution must be decanted, and boiled to dryness in a glass vessel. A white mass will remain, which may be fused in a platinum crucible, and poured out into a clean copper dish. A transparent substance is thus obtained, consisting of phosphoric acid, with phosphate, and a little sulphate of lime, commonly known under the name of *glass of phosphorus*. It yields phosphorus when distilled at a bright red heat with charcoal, in the way above described; but when any quantity of phosphorus is to be collected, the retort should be very well and carefully luted, and should have a wide neck terminating in a copper tube, so bent as to dip perpendicularly into a bottle of water, otherwise it will be apt to become plugged up by congealed phosphorus. The phosphorus is generally sufficiently purified by fusing it in hot water, and when cold, cutting it into small pieces, which are put with water into a slightly conical glass tube, and fused by immersion in hot water: on cooling, the phosphorus is withdrawn in the form of a stick. If the phosphorus is much discoloured, it may be cleansed by fusing it first in warm caustic ammonia, and then in alcohol.

“Wöhler recommends instead of the preceding process, to calcine ivory black (which is a mixture of phosphate of lime and charcoal), with fine quartz sand and a little ordinary charcoal, in cylinders of fire-clay, at a very high temperature. Each cylinder has a bent copper tube adapted to it, one branch of which descends into a vessel containing water. The efficiency of this process depends upon the silica acting as an acid and combining with the lime of the phosphate at a high temperature, while the liberated phosphoric acid is decomposed by the carbon.” (GRAHAM.)

When pure, phosphorus is tasteless, colourless, or of a pale buff colour, semitransparent, and flexible at common temperatures, but at 32° , crystalline and brittle. It is also rendered brittle by the presence of less than a 200th part of sulphur. Its specific gravity is 1.770. Its specific heat, as ascertained, apparently with accuracy, by Regnault, is 0.1887, but Dulong and Petit give 0.385 as the average result of their experiments. (*Ann. Chim. & Phys.*, lxxiii. 55.) It is insoluble in water. It melts, when air is excluded, at 105° , undergoing a remarkable dilatation of 0.031 of its volume. If suddenly cooled to 32° , after having been heated to 140° , it sometimes becomes black (THENARD); but if slowly cooled, always remains colourless. “When fused and left undisturbed, it sometimes remains liquid for hours at the usual temperature, particularly when covered by an alkaline liquid.” (GRAHAM.) Under these circumstances its temperature suddenly rises in the act of solidification to about

100°. (DUMAS.) At 550° it boils, air being excluded, and rapidly evaporates in the form of colourless vapour, the density of which, according to Dumas, is 4.355. But phosphorus evaporates, especially if in contact with moisture, at a much lower temperature. The volatility of phosphorus in conjunction with aqueous vapour is well shown by boiling a flask of water containing a piece of phosphorus, over a lamp; the vapour, as it issues from the flask, is beautifully luminous in a dark room. Phosphorus may be purified by careful distillation, but the process is troublesome and dangerous. Dr. Henry gives the following directions for it:—The proper quantity of phosphorus should first be put into the retort, with a sufficient portion of water to cover it. The water must then be made hot enough to melt the phosphorus, which, on cooling, forms a mass, of the shape of the bottom of the retort. When cold, fill the retort with water, and invert it in water. Displace the water by hydrogen gas, forced from a bladder through a bent pipe; keep the finger on the open end of the retort neck; place it in a sand-bath; and immerse the mouth of it in water. Then apply heat very cautiously. A bladder should also be provided, furnished with a stop-cock and pipe, and filled with hydrogen. During the distillation, the gas in the retort is absorbed, and it is necessary to add more from the bladder, otherwise the water will rush into the retort, and occasion an explosion. By distillation in this mode, phosphorus is rendered much purer. In the neck of the retort a substance is condensed of a beautiful red or carmine colour, which is a combination of carbon and phosphorus, or a *phosphuret of carbon*. Thenard observes that phosphorus, however frequently distilled, cannot be freed entirely from carbon, a minute quantity of which does not impair its colour or transparency.

When phosphorus is fused with about half its weight of sulphur, and suffered to cool gradually, a part of the phosphorus separates in rhombic dodecaëdral crystals. (MITSCHERLICH, *Ann. de Chim. et Phys.*, vol. xxiv. p. 270.) It may also be crystallized by slowly cooling a saturated solution of it in naphtha. When exposed to air, it exhales luminous fumes, having a peculiar alliaceous odour: this arises from a slow combustion; hence the necessity of preserving it in water. It has been used in medicine in doses of from one to six grains in the course of the day, dissolved in oil or ether, and is said to be a powerful restorative. In over-doses it is poisonous. (ORFILA, *Traité des Poisons*, ii. Dr. C. W. GREGORY on *New Remedies*.)

Retained for some time in contact with water, phosphorus decomposes it; oxide of phosphorus, and, probably, phosphorous and phosphoric acids are formed, and phosphuretted hydrogen is emitted. Mr. Phillips has observed that these changes are most rapid when light has free access. (*Ann. of Philos.*, vol. v.) According to Berzelius, light, and especially violet light, has the peculiar effect of reddening phosphorus under whatever circumstances it is exposed to its influence; in nitrogen gas, the concentrated solar rays readily fuse it, but in hydrogen and in vacuo, they cause it to sublime in red scales. There are several peculiar circumstances respecting the luminosity and inflammability of phosphorus. When exposed to the air at temperatures above the freezing point, it shines in the dark with a pale blue light, which increases in intensity with the

Lumy.

temperature. This appears to arise from a very slow combustion, attended by the production of acid: it ceases in close vessels as soon as the greater part of the oxygen has been absorbed; and is said not to take place when the air has been artificially dried: in this case the requisite formation of phosphorous acid seems to be prevented. In pure oxygen, phosphorus is not luminous till heated to between 70° and 80° , above which it becomes very luminous, and soon inflames. Oxygen, and most other gases, in which phosphorus has been immersed, acquire its odour, and when mixed with air become slightly luminous. According to Dr. Henry, if a piece of phosphorus be introduced into a vessel of oxygen gas over mercury, at a temperature not exceeding 80° , no perceptible absorption will happen in twenty-four hours; but if, the temperature remaining the same, the pressure be diminished to one-eighth or one-tenth that of the atmosphere, the phosphorus will be surrounded with white vapours, will become luminous in the dark, and will absorb oxygen. Under ordinary pressures, a higher temperature is required for this effect; but if the density of the oxygen be reduced in the above proportion by mixing it with nitrogen, hydrogen, or carbonic acid, the phosphorus becomes luminous. Mr. Graham has shown that the slow combustion of phosphorus in air, is prevented by very small additions of certain gases and vapours. (*Quart. Journ., N. S.*, vol. vi. p. 83.) Thus at the temperature of 66° it is entirely prevented by one volume of olefant gas in 450 volumes of air, by one volume of ether vapour in 150 volumes of air, by one volume of naphtha vapour in 1820, and of oil of turpentine vapour in 4444 volumes of air. This influence is not confined to low temperatures, for a certain admixture of the above vapours will even prevent the oxidation of phosphorus at 200° ; but on allowing such gaseous mixtures to expand, by diminishing the pressure upon them, the phosphorus becomes luminous, and the proportion of foreign gas required to prevent oxidation or slow combustion must be much increased. "The only explanation," Mr. Graham observes, "of this phenomenon which can be offered, is that the gases which exert this influence have an attraction for oxygen, and there is reason to believe are themselves undergoing a slow oxidation at the same time. Now when two oxidable bodies are in contact, one of them often takes precedence in combining with oxygen to the entire exclusion of the other. Potassium is defended from oxidation in air by the same vapours, though to a less degree."

In the vacuum of the air-pump, phosphorus in small pieces, loosely enveloped in cotton, will generally inflame and burn for a time with a pale light: under the same circumstances it more readily kindles if sprinkled with powdered resin or sulphur; alone, it does not inflame. When a stick of phosphorus is sprinkled with lampblack, or powdered animal charcoal, it is also apt to inflame; and, what is curious, when very thin slices of phosphorus are placed upon flannel, wool, lint, fine feathers, or other downy and flocculent substances, they fuse and readily inflame upon the gentlest friction. It seems as if the slow combustion of the phosphorus produced heat enough to fuse it whilst lying upon a very bad conductor. Berzelius remarks, that the water in which phosphorus has been kept in perfectly closed vessels, acquires a luminous property when agitated; this is not the case when air has access.

The temperature at which phosphorus inflames has been variously stated. According to Dr. Higgins, when perfectly dry, a temperature of 60° is sufficient. It easily takes fire by the heat of the hand and slight friction, or when rubbed upon a piece of coarse paper: it requires therefore to be handled and wiped with the utmost caution. Owing to the superficial formation of phosphorous and phosphoric acid, when it burns imperfectly at low temperatures, its further combustion is often prevented: thus, in rubbing a fragment of phosphorus between two pieces of brown paper, a momentary combustion often ensues, and it requires considerable friction to cause it again to inflame; for the same reason it is very difficult to light a piece of paper by the flame of phosphorus, for the paper becomes covered and protected by the acid.

PHOSPHORUS AND OXYGEN.—At a temperature of about 120° , phosphorus instantly takes fire, and burns with intense brilliancy, throwing off copious white fumes of phosphoric acid. If, instead of burning phosphorus with free access of air, it be heated in a confined portion of very rare air, it enters into less perfect combustion, and three compounds of phosphorus with oxygen are the result, each characterized by distinct properties. The first is a red solid, less fusible than phosphorus; the second is a white substance, more volatile than phosphorus; the third, a white and more fixed body. The red solid consists of a mixture of phosphorus and oxide of phosphorus.

OXIDE OF PHOSPHORUS. ($3p + o$).—The white substance with which phosphorus becomes incrustated when kept for some time in water, is generally stated to be an oxide of phosphorus, but Rose has thrown some doubt upon this opinion (POGGEND. xxvii. 565), and Pelouze considers it as a *hydrate* of phosphorus. ($4p + q$.) The red solid is very inflammable, and less fusible and volatile than phosphorus. It is this substance which is generally used in the *phosphoric match-boxes*. To prepare it for this purpose a piece of phosphorus may be put into a small phial, and melted and stirred about with a hot iron-wire, so as to coat its interior. A portion of the phosphorus is thus oxidized by its imperfect combustion, and a small quantity, taken out upon the end of a brimstone match, instantly inflames upon coming into the contact of the air. (NICHOLSON'S *Journal*, vi. 134.)

According to Pelouze (*Ann. de Chim. et Phys.*, L. 83), an oxide of phosphorus is formed by throwing a jet of oxygen gas into phosphorus fused under hot water; vivid combustion ensues, and phosphoric acid is formed, and at the same time a red pulverulent oxide deposited, which is insoluble in water, ether, alcohol, and oils, difficultly inflammable when heated in the air, but instantly burning upon contact of nitric acid. It appears to consist of

						Pelouze.
Phosphorus	3 . . . 48 . . . 85.71	85.5
Oxygen	1 . . . 8 . . . 14.29	14.5
<hr/>						
Oxide of phosphorus	1			56	100.00	100.0

According to Le Verrier, a definite oxide of phosphorus, consisting of

2 atoms of phosphorus + 1 of oxygen, is obtained by exposing small fragments of phosphorus, covered by the liquid chloride of phosphorus, to the action of air: phosphoric acid is formed, and at the same time a yellowish substance, which he regards as a phosphate of the above oxide of phosphorus, and which yields a yellow solution with water. At a temperature of about 176° this solution is decomposed, and a yellow flocculent substance subsides, which is a hydrated oxide of phosphorus, but which, when dried in vacuo over sulphuric acid, loses its combined water. In this state it is a yellow powder insoluble in water, alcohol, and ether. It resists a temperature of 570° without decomposition, but acquires a red colour: it does not burn till heated somewhat beyond the boiling point of mercury. It appears to form feeble combinations with the alkaline salifiable bases.

There are three *acid* compounds of phosphorus and oxygen, which have been termed *hypophosphorous*, *phosphorous*, and *phosphoric* acids.

HYPOPHOSPHOROUS ACID. ($2p + o$) or \underline{p} , was discovered by Dulong in 1816. (*Ann. de Chim. et Phys.*, ii. 141.) It is prepared as follows: Upon 1 part of *phosphuret of barium* pour 4 parts of water, and when the evolution of phosphuretted hydrogen gas has ceased, pour the whole upon a filter. To the filtered liquid add sulphuric acid as long as any precipitate forms: separate the precipitate, which is a compound of sulphuric acid and baryta, and the clear liquor now contains the hypophosphorous acid in solution. When concentrated by evaporation, a sour viscid liquid is obtained, incapable of crystallization, and eagerly attractive of oxygen.

Rose obtained pure hypophosphorous acid by boiling hydrate of baryta with water and phosphorus, till all garlic odour ceased, filtering the liquid and decomposing it by excess of sulphuric acid; separating the precipitate and digesting the clear fluid for a short time with excess of oxide of lead; then filtering the sulphate of lead from the solution of *hypophosphite of lead*, and decomposing the latter by a current of sulphuretted hydrogen. The acid, freed from the precipitate, was concentrated until of sufficient strength.

Hypophosphorous acid appears to consist of 2 atoms of phosphorus and 1 of oxygen.

Phosphorus	2	32	80	Dulong.
Oxygen	1	8	20	73.4
Hypophosphorous acid	1	40	100	26.6
				100.0

But its true atomic weight cannot be accurately determined till the composition of the *hypophosphites* is better known.

When hypophosphorous acid is heated, it is decomposed with the evolution of phosphuretted hydrogen and phosphorus; phosphoric acid is the residue: in its ordinary state, therefore, it evidently contains combined water, and indeed it yields a crystallizable hydrate by very cautious evaporation. It is a powerful deoxidizing agent. In combination with bases it forms *hypophosphites*; they are soluble in water, and many of them in alcohol; they are decomposed by a red heat: they are mostly deliquescent and uncrystallizable. (DULONG.)

HYPOPHOSPHITE OF AMMONIA.—This salt is extremely soluble, very deliquescent, very difficultly crystallizable, and soluble in alcohol.

PHOSPHOROUS ACID. ($p + 1\frac{1}{2}o$) or \hat{p} .—The volatile white substance above mentioned as one of the products of the combustion of phosphorus in rarefied air, is this acid in a dry state: by burning phosphorus in a tube with very limited access of air, and caution as to temperature, as for instance, by placing a piece of phosphorus near one end of a tube three feet long, inflaming it, and gently propelling air through the tube, it may be collected in the form of a white volatile powder, which, when exposed to air, rapidly absorbs moisture, becomes hot, inflames, and burns into phosphoric acid. Heated in close vessels it gives off phosphorus and leaves phosphoric acid. It rapidly dissolves in water, has a sour taste, reddens vegetable blues, and combines with certain of the salifiable bases to form salts called *phosphites*. When acted upon by such of the metallic oxides as readily part with their oxygen, it is converted into phosphoric acid, and the oxide is reduced.

The phosphorous acid in combination with a definite proportion of water, forming what Sir H. Davy termed *hydrophosphorous acid*, is obtained by mixing *protochloride of phosphorus* with water: a mutual decomposition of the liquids ensues, and hydrochloric acid and phosphorous acid result; the former is easily driven off by heat, and, on carefully evaporating the remaining solution, a crystallizable compound is obtained, of a sour taste, and very soluble in water, which by heat is resolved into phosphoric acid and hydroguret of phosphorus. (See *Phosphuretted Hydrogen*.) A current of chlorine passed through phosphorus fused under hot water, first converts it into a chloride, which afterwards reacts on the water: on evaporation, the hydrophosphorous acid remains.

The slow and spontaneous combustion of phosphorus in a moist atmosphere, as when phosphorus is suffered to deliquesce upon a funnel, is attended by the production of a sour liquid, which may thus be gradually collected; it appears to be a mixture of hydrated phosphorous and phosphoric acids. Dulong termed it *phosphatic acid*.

If the equivalent of the phosphorous acid be deduced from its saturating power, the phosphites being regarded as constituted of one atom of acid united to one atom of base, it will consist of

				Davy.	Berzelius.	Dulong.
Phosphorus . . .	1	16	57.14	56	56.524	57.18
Oxygen . . .	$1\frac{1}{2}$	12	42.86	44	43.476	42.82
Phosphorous acid	1	28	100.00	100	100.000	100.00

PHOSPHITE OF AMMONIA. ($\hat{p} + A.$)—This salt is obtained in deliquescent prismatic crystals by saturating phosphorous acid with carbonate of ammonia. When heated it gives out ammonia, and leaves phosphorous acid and water, which, on the further application of heat, is decomposed, and hydrated phosphoric acid remains. (ROSE, POGG., *Ann.*, ix. 28.) According to Dr. Thomson, the constituents of the crystals are

Ammonia	1	17	27.0
Phosphorous acid . . .	1	28	44.4
Water	2	18	28.6
Phosphite of ammonia	1	63	100.0

PHOSPHORIC ACID. ($p + 2\frac{1}{2}O$) or p' . $2P^5O$, or \ddot{P} , TURNER. ($p + 5O$) or PO_5 , GRAHAM*.—This acid may be formed by the direct combustion of phosphorus in excess of oxygen; intense heat and light are produced, and white deliquescent flocculi line the interior of the receiver. It is produced in the same way by burning phosphorus under a dry bell-glass in atmospheric air. For this purpose, a piece of phosphorus, in a watch-glass or small porcelain capsule, may be placed upon a plate of glass, and covered over with a tall receiver; when inflamed, it burns at first furiously, but the combustion gradually subsides for want of oxygen, and may be renewed by gently lifting the receiver off the glass plate: thus the whole of the phosphorus may be gradually burned, and it forms a quantity of dense smoke, which subsides in the form of snowy flakes: this is *Anhydrous Phosphoric Acid*, mixed sometimes with a little phosphorous acid: if water be dropped upon it, it produces a hissing noise, and much heat is evolved, but it is some time before the whole dissolves into a clear liquid. The solution is intensely sour. In its anhydrous state this acid appears to be perfectly fixed, but in the air, or wherever aqueous vapour is present, it sublimes away, apparently in the state of hydrate.

Phosphoric acid may also be obtained by acting upon phosphorus by nitric acid; in this case, if the action be at all intense, a portion of ammonia is at the same time produced, which is found in the state of phosphate of ammonia in solution. About six parts of nitric acid, specific gravity 1.4, are introduced into a tubulated retort placed in a sand-heat, with a tubulated receiver luted on to it, the stopper of which should be open. When the acid is warm, drop into it gradually and carefully one part of phosphorus in small pieces; red nitrous vapour is instantly disengaged, and when its evolution ceases, put the stopper loosely into the receiver, and distil till the residue in the retort acquires the consistence of syrup; pour it into a platinum crucible, and give it a dull red heat; it fuses, and concretes on cooling, into a transparent substance, which is *hydrated phosphoric acid*, and which retains water with great avidity, even at red heat, and at very high temperatures slowly volatilizes; in this state it is sometimes called *glacial phosphoric acid*. In the *London Pharmacopæia* diluted phosphoric acid is directed to be obtained by distilling a mixture of 4 fluid ounces of nitric acid and 10 of water, off an ounce of phosphorus: when 8 fluid ounces have passed over they are to be returned into the retort and again distilled over; the remaining liquor is then to be evaporated in a platinum capsule and diluted with distilled water, so as to make up 28 fluid ounces. The specific gravity of this dilute acid is 1.064, and 100 grains of it are saturated by 42 of crystallized carbonate of soda: it appears to contain about 10 per cent. of acid.

* Professor Graham, to whom we are indebted for an elaborate investigation into the constitution of the modifications of this acid and the atomic composition of the phosphates, doubles the equivalent of phosphorus, and represents this acid, therefore, as a compound of 1 atom

of phosphorus and 5 of oxygen. Dr. Turner, on the other hand, represents it as constituted of 2 atoms of phosphorus and 5 of oxygen, in this case retaining the equivalent 16 (or 15.7) for phosphorus, whereas Graham uses 31.4 (nearly 16×2) as the equivalent of phosphorus.

Another mode of obtaining phosphoric acid, consists in heating *phosphate of ammonia* to redness, which may be economically prepared for this purpose by saturating the impure phosphoric acid obtained from calcined bones (p. 484) by carbonate of ammonia.

The hydrated phosphoric acid, when pure, readily dissolves in water; it deliquesces upon exposure to humid air into an intensely sour liquid, of a specific gravity = 2. It does not corrode the skin like nitric and sulphuric acids. Dr. Turner remarks (*Elements of Chemistry*), that it may be distinguished from all other acids by the following circumstances: that when carefully neutralized by pure carbonate of soda or potassa, it forms a solution in which no precipitate, or change of colour, is produced, when a stream of sulphuretted hydrogen gas is passed through it; but which is precipitated *white* by a solution of acetate of lead, and *yellow* by nitrate of silver: the first precipitate, the phosphate of lead, dissolves completely on the addition of nitric or phosphoric acid; the second, the phosphate of silver, is dissolved by both these acids and by ammonia.

It has been satisfactorily proved by the accurate researches of Berzelius and of Dulong, that the ratio of the oxygen in the phosphorous acid is to that in the phosphoric acid as 3 to 5; and assuming these acids to consist respectively of one atom of phosphorus and three of oxygen, and one atom of phosphorus and five of oxygen, the number 32 (or thereabout) would be the equivalent of phosphorus, and 72 that of the phosphoric acid; but the adoption of this latter number would oblige us to consider the *neutral* phosphates as constituted of *one* atom of acid and *two* atoms of base, which is contrary to all analogy; the fact is, that 36 is the equivalent of the phosphoric acid, and 28 that of the phosphorous acid; hence the necessity of considering the latter, as above stated, a compound of 1 atom of phosphorus and $1\frac{1}{2}$ of oxygen; and upon the same principle the anhydrous phosphoric acid will consist of

				Davy.	Berzelius.	Dulong.	Rosc.
Phosphorus . . .	1	16	44.44	42.6	43.823	44.8	46.5
Oxygen . . .	$2\frac{1}{2}$	20	55.56	57.4	56.177	55.2	53.5
Phosphoric acid	1	36	100.00	100.0	100.000	100.0	100.0

The *glacial phosphoric acid*, or the hydrated acid exposed to a heat at which it no longer loses water, but begins to sublime or evaporate without decomposition, appears to consist of

				Dulong.
Phosphoric acid . . .	1	36	80	79.4
Water	1	9	20	20.6
Glacial phosphoric acid	1	45	100	100.0

Mr. Graham observes (*Elements of Chemistry*) that when phosphoric acid is dissolved in water the compound is marked by an unusual inconstancy of character, arising from the circumstance that it is not actual phosphoric acid, but a hydrate of that acid, which is soluble, as indeed is also the case with sulphuric acid; but the peculiarities of the phosphoric acid arise out of the circumstance that it forms *three* definite combinations with water, each of which is soluble without change, and these *phos-*

phates of water exhibit properties so distinct that they might be supposed to contain distinct acids. When the anhydrous acid obtained by burning phosphorus in dry air is thrown into water, it produces an indefinite mixture of the three hydrates, but each of them may be obtained pure by a particular process, in reference to which I shall adopt Mr. Graham's nomenclature.

1. *Terhydrate, or Tribasic Phosphate of Water.* $3\text{HO} + \text{PO}_5$. ($= 1\frac{1}{2}(h+o) + (p+2\frac{1}{2}o)$ of our equivalents; or 1 atom of anhydrous phosphoric acid and $1\frac{1}{2}$ of water.)—This compound is obtained by adding to a warm solution of the common phosphate of soda of pharmacy (which should be re-crystallized in order to purify it) a solution of acetate of lead, so long as it occasions a precipitate: the phosphate of lead which falls is then washed, diffused in cold water, and decomposed by a stream of sulphuretted hydrogen; the liquor is then heated and filtered; it is very sour and contains the terhydrate of phosphoric acid. "The characters of this solution are to give a *yellow* precipitate with nitrate of silver, to yield the common phosphate of soda when neutralized by carbonate of soda, to form salts which have invariably three atoms of base to one of phosphoric acid, and to be unalterable by boiling its solution, or keeping it for any length of time. The class of salts which this hydrate forms are the old phosphates which have been long known, and it is convenient to allow them to be particularly distinguished as the *phosphates*, or common phosphates." In the language of our equivalents it is a *sesquihydrate*.

2. *Deutohydrate of Phosphoric Acid, or Bibasic Phosphate of Water.* $2\text{HO} + \text{PO}_5$. ($= (h+o) + (p+2\frac{1}{2}o)$ of our equivalents; or 1 atom of anhydrous phosphoric acid and 1 of water.) *Pyrophosphoric Acid.*—In the year 1826, Dr. Clark, of Glasgow, observed, that when *phosphate of soda* had been heated to redness, its solution, instead of throwing down a yellow precipitate with nitrate of silver, produced a *white* precipitate. (BREWSTER'S *Edin. Journal*, vii. 298.) Professor Stromeyer had also observed the same fact, and in 1830, communicated a paper on the subject to the Royal Society of Göttingen. (*Ann. de Chim. et Phys.*, xliii. 364.) The phosphoric acid, after it has been exposed for some time to heat, yields, when saturated with bases, salts possessed of certain peculiarities, which have hence been termed *pyrophosphates*. If a solution of such pyrophosphate of soda be precipitated by acetate of lead, the precipitate washed and decomposed by sulphuretted hydrogen as before, an acid liquor is obtained, which holds the deutohydrate of phosphoric acid in solution; it must not be heated to expel the sulphuretted hydrogen, but left in a shallow basin for 24 hours to allow the escape of that gas. The acid thus obtained gives a *white* precipitate with nitrate of silver; when neutralized by carbonate of soda it gives Dr. Clark's pyrophosphate of soda, and all the salts which it forms have uniformly 2 atoms of base (in reference, that is, to Mr. Graham's equivalents). These salts may by way of distinction, be denominated *pyrophosphates*. A dilute solution of the pyrophosphoric acid may be preserved without change, but if boiled it passes into the terhydrate (or sesquihydrate of our equivalents).

3. *Protohydrate of Phosphoric Acid.* $\text{HO} + \text{PO}_5$ (GRAHAM), or

$(h + o) + 2(p + 2\frac{1}{2}o)$, that is, 2 atoms of anhydrous acid and 1 of water, according to our equivalents. This modification of the phosphoric acid is obtained by heating biphosphate of soda to redness, dissolving it in water, and decomposing the solution by acetate of lead: the precipitate is then to be treated by sulphuretted hydrogen as before, and the resulting acid liquor contains Graham's protohydrate of phosphoric acid. The biphosphate of soda for this purpose is prepared by adding a solution of the terhydrate of phosphoric acid to a solution of the common phosphate of soda, till a drop of the latter is no longer precipitated by chloride of barium: the biphosphate of soda, now in solution, can only be crystallized in cold weather. "This acid is characterized," says Mr. Graham, "by producing a white precipitate in solution of albumen; and in solutions of the salts of earths and metallic oxides, precipitates which are remarkable semifluid bodies, or soft solids, without crystallization. All these salts contain only one atom of base to one of acid, like the protohydrate of the acid itself. (The trivial name *metaphosphates* was applied to the class by myself to mark the cause of the retention of peculiar properties by their acid, when free and in solution, namely, that it was not then simply phosphoric acid but phosphoric acid *together with water*. *Phil. Trans.*, 1833, p. 253.) This is the least stable of the hydrates of phosphoric acid, being converted rapidly by the ebullition of its solution into the terhydrate. If the terms *metaphosphoric* and *pyrophosphoric acid* are employed at all, it is to be remembered that they are applicable to the proto and deutohydrates, and not to the acid itself, which is the same in all the hydrates. But to prevent the chance of misconception, *metaphosphate of water* and *pyrophosphate of water* might be substituted for these terms."

We shall find in the sequel that the three hydrates of phosphoric acid form three classes of phosphates, the quantity of base which unites to the acid in the humid way being regulated by the proportion of water previously combined with the acid, and which is replaced by the fixed base, affording, as Mr. Graham observes, a good illustration of the formation of compounds by substitution. Thus, "The protohydrate of phosphoric acid combines with no more than one, and the deutohydrate with no more than two, proportions of soda, although three or a larger number of proportions of alkali be added to it: the excess of alkali remains free." Mr. Graham's further remarks upon this curious and intricate subject I must leave till the other salts of the phosphoric acid are individually before us; in the mean time, I must again remind the student of the discrepancy between Mr. Graham's equivalents and those which we have adopted, in respect to the phosphoric acid, *two* of our equivalents of that acid being = to *one* of his, whilst our equivalents for water agree; and although Dr. Turner and Mr. Graham agree in their equivalent number for phosphoric acid, they give different views of its atomic constitution, Turner representing it as constituted of 2 atoms of phosphorus and 5 of oxygen, (simply, therefore, doubling our numbers,) whilst Graham doubles the number for phosphorus, and therefore represents phosphoric acid as constituted of 1 atom of phosphorus and 5 of oxygen. The following is a comparative statement of these different views:—

GRAHAM.		TURNER.		BRANDE.	
	Symbol.	Equivalent.	Symbol.	Equivalent.	
Phosphorus	P	31.44	P	15.72	p 16
Anhydrous phosphoric acid.	PO ₅	71.44	P ₂ O ₅	71.44	(p + 2½o) 36
Protohydrate of phosphoric acid: monobasic phosphate of water: metaphosphate of water . . .	HO + PO ₅	-	HO + P ₂ O ₅	-	(h + o) + 2(p + 2½o) - {Dibasic phosphate of water.
Deutohydrate of phosphoric acid: bibasic phosphate of water: pyrophosphate of water	2HO + PO ₅	-	2HO + P ₂ O ₅	-	(h + o) + (p + 2½o) - {Monobasic phosphate of water.
Terhydrate of phosphoric acid: tribasic phosphate of water: phosphate of water	3HO + PO ₅	-	3HO + P ₂ O ₅	-	1½(h + o) + (p + 2½o) - {Sesquibasic phosphate of water.

PHOSPHATE OF AMMONIA. ($p' + A.$)—The mutual action of anhydrous phosphoric acid and ammonia has not been studied: they probably give rise to an *amide*. The neutral phosphate of ammonia may be obtained pure by saturating phosphoric acid with ammonia or carbonate of ammonia and carefully evaporating, so as to avoid the production of an acid salt. It may also be formed by adding carbonate of ammonia to the acid phosphate of lime obtained from bone earth (p. 484), till no further effervescence or precipitation of phosphate of lime follows, filtering and evaporating, taking care, however, to leave slight excess of ammonia: the solution left to itself deposits the salt. Its primary form is an oblique rhombic prism, the smaller angle of which is $84^{\circ} 30'$. Its prisms are often terminated by dièdral summits. (MITSCHERLICH, *Ann. de Chim. et Phys.*, xix. 382.) The crystals are efflorescent, and by long exposure become *biphosphate* from loss of ammonia: they taste saline, cooling, and bitterish. This salt is soluble in 4 parts of cold water. When heated it melts, and losing ammonia leaves hydrated phosphoric acid. It exists in the urine of carnivorous animals. This salt has not been accurately analyzed, but it probably consists of

					Mitscherlich.
Ammonia	1	. .	17	. .	25.57
Phosphoric acid	1	. .	36	. .	54.13
Water	$1\frac{1}{2}$. .	13.5	. .	20.30
<hr/>					
Phosphate of ammonia	1		66.5		100.00

BIPHOSPHATE OF AMMONIA. ($2p' + A.$)—This salt is obtained by adding phosphoric acid to a solution of the phosphate of ammonia till it strongly reddens litmus paper, and ceases to occasion a precipitate in a dilute solution of chloride of barium. When the solution is concentrated it yields crystals, the primary form of which is an octoëdron with a square base; but they are most commonly right square prisms terminated by the primary faces. They are less soluble than the preceding salt, and permanent in the air: when heated they fuse and froth up, ultimately leaving hydrated phosphoric acid. They consist of

					Mitscherlich.
Ammonia	1	. .	17	. .	14.65
Phosphoric acid	2	. .	72	. .	62.07
Water	3	. .	27	. .	23.28
<hr/>					
Biphosphate of ammonia	1		116		100.00

Gay Lussac has recommended the application of phosphate of ammonia to render muslin, and similar articles of clothing, to a considerable extent incombustible. The goods are immersed in a solution of equal parts of phosphate and hydrochlorate of ammonia of a due strength, and then dried; upon applying flame to them, it will be found that they are burned with great difficulty, and cannot be consumed with flame, in consequence of the prevention of the access of oxygen by the glazing which the salts form at high temperatures.

When considering the basic oxides, the constitution of the *phosphates* will be more particularly adverted to. Mr. Graham's views respecting the peculiarities of these salts, as formed by the three hydrates of phosphoric acid, will be found in his *Elements of Chemistry*, p. 349.

PHOSPHORUS AND CHLORINE.—These elements unite in two proportions, forming two definite compounds, the *chloride*, or *sesquichloride*, and the *perchloride* of phosphorus.

PROTOCHLORIDE OF PHOSPHORUS. SESQUICHLORIDE OF PHOSPHORUS. (TERCHLORIDE OF PHOSPHORUS. GRAHAM.) $(p + 1\frac{1}{2}c)$ or $(2p + 3c)$.—This compound is procured by distilling a mixture of phosphorus and *perchloride of mercury*; or, what amounts to the same thing, by passing the vapour of phosphorus over perchloride of mercury in a heated glass tube, terminating in a cooled receiver. It is also formed by passing chlorine first through a cold flask, then through a tube containing fragments of fused chloride of calcium, and thence into a tubulated retort, slightly warmed, and containing phosphorus, from which the sesquichloride, as it is formed, gradually distils over into a cooled receiver. (GMELIN.)

When first obtained, this compound generally holds a little phosphorus in solution, which gives it a reddish colour; this is in time deposited, and it becomes limpid and colourless; or it may at once be purified by slow distillation; it requires to be cautiously excluded from the action of the air. It has a suffocating odour. Its specific gravity is 1.45. Exposed to the air it exhales acid fumes: it does not change the colour of *dry* vegetable blues, but becomes powerfully acid upon the least acquisition of moisture. Its vapour is combustible. Chlorine converts it into perchloride of phosphorus. It acts upon water with great energy, and produces hydrochloric and *phosphorous* acids, as above stated (page 489).

It appears from the analyses of Davy and of Berzelius, that this chloride corresponds in composition to the phosphorous acid; it is therefore a sesquichloride of phosphorus, and consists of

						Davy and Berzelius.
Phosphorus	1	. .	16	. .	22.9 . . 23
Chlorine	$1\frac{1}{2}$. .	54	. .	77.1 . . 77
<hr/>				<hr/>		
Sesquichloride of Phosphorus	1			70		100.0 . . 100

PERCHLORIDE OF PHOSPHORUS. $(p + 2\frac{1}{2}c)$ or $(2p + 5c)$.—When phosphorus is submitted to the action of chlorine in excess, it burns with a pale yellow flame, and produces a white, flaky, and volatile compound, which attaches itself to the interior of the vessel, and which is the *perchloride of phosphorus*. It may be conveniently formed in the exhausted retort, as described at p. 364. It was long mistaken for phosphoric acid, but its easy volatility is alone sufficient distinction, for it rises in vapour at 200° . It is fusible under pressure, and crystallizable in transparent prisms; it is a non-conductor of electricity; it reddens dry litmus paper, in consequence, as Berzelius supposes, of its acquiring hydrogen and oxygen from the decomposition of the paper. It fumes in the air, and when brought into the contact of water, a mutual decomposition is immediately effected, and phosphoric and hydrochloric acids result. When passed through a red-hot porcelain tube with oxygen, phosphoric acid is produced and chlorine evolved, which shows that oxygen, at that temperature, has a stronger attraction for phosphorus than chlorine. Potassium, heated in its vapour, burns with great brilliancy:

the metallic oxides decompose it with the production of metallic chlorides and phosphates.

The perchloride of phosphorus consists of

				Davy.			Dulong.			Berzelius.		
Phosphorus	1	..	16	..	15.1	..	13	..	15.4	..	15.31	
Chlorine	2 $\frac{1}{2}$..	90	..	84.9	..	87	..	84.6	..	84.69	
Perchloride of phosphorus	1		106		100.0		100		100.0		100.00	

AMMONIA AND CHLORIDE OF PHOSPHORUS.—*The action of ammonia on the chlorides of phosphorus* is very remarkable, and was first observed by Davy, and since elaborately examined by H. Rose. When ammonia is admitted into an exhausted retort containing the perchloride of phosphorus, the gas is rapidly absorbed with much heat, and a compound is produced which, according to Davy, is insoluble in water, indecomposable by acid or alkaline solutions, and has characters analogous to an earth. The action of ammonia on the sesquichloride is attended by the production of the same compound, and the separation of a portion of phosphorus. (*Elements*, p. 291.) According to H. Rose, (*über eine Verbindung des Phosphors mit dem Stickstoff*;) the most definite action of ammonia is on the sesquichloride of phosphorus. (POGGEND., xxiv. 308.) This liquid, when freed from dissolved phosphorus by repeated distillation, and subjected (surrounded by a freezing mixture so as to prevent elevation of temperature and consequent deposition of phosphorus) to the gradual action of excess of ammonia, forms with it a perfectly white compound, which is entirely, though very slowly, soluble in water, and is so constituted, as to yield in this process, neutral hydrochlorate and phosphite of ammonia. When heated in the air, it gives off hydrochlorate of ammonia, and leaves an insoluble reddish-brown substance, which, when heated, becomes white, but again brown as it cools. To obtain the fixed residue in a pure state, freshly prepared *ammonio-sesquichloride of phosphorus* must be cautiously heated to redness out of the contact of air: this is best done by putting it into a sufficiently large tube of difficultly fusible glass, and passing over it at a red heat a stream of carbonic-acid gas dried by contact of chloride of calcium: the operation must be patiently carried on till no traces of hydrochlorate of ammonia are evolved. With these precautions, the substance which remains is a light white powder, and though formed of highly-volatile substances is, when excluded from air and moisture, fixed and infusible at a red heat: heated in contact of the air and its moisture, it evolves white fumes of phosphoric acid, and becomes slowly oxidized without flaming: if thus heated in a platinum crucible, the metal is much corroded. Exclusively of its fixedness out of the contact of air, the most remarkable property of this substance is its indifference to the strongest re-agents. Concentrated nitric acid very slowly converts a portion of it into phosphoric acid, and concentrated sulphuric acid produces the same change with the evolution of sulphurous acid; but the dilute acids and alkaline solutions, and chlorine, sulphur, and carbonic acid, have no action upon it even when heated. It is, on the contrary, energetically acted upon when fused with caustic potassa; ammonia is evolved, and the residue is soluble in water. It is decomposed when heated with hydrate of baryta, with intense ignition:

it is also decomposed by fusion with the carbonated fixed alkalis, and with their nitrates. The action of dry hydrogen gas upon this compound at a red heat is very remarkable; no trace of water is formed, phosphorus is evolved, and distils off, and on conducting the gaseous products into water, ammonia is found in solution. From this result, and from other evidence adduced by Rose, this compound apparently consists of phosphorus and nitrogen; it is a true *phosphuret of nitrogen*; and from the analytical details given at length in the essay I have quoted, it appears that 100 parts of the ammonio-sesquichloride, yield an average product of 21·27 of this phosphuret of nitrogen, and that it consists of

					Rose.
Phosphorus . . .	1	..	16	..	53·3
Nitrogen . . .	1	..	14	..	46·7
					52·56
					47·44
Phosphuret of nitrogen	1		30		100·0
					100·00

It is obvious that there is no analogy between this compound and those of nitrogen with chlorine and iodine; indeed, its properties are diametrically opposed to those detonating and easily-decomposable substances: it presents a remarkable but not solitary instance of the production of a fixed substance from the union of highly volatile elements. Its atomic constitution as given above, closely agrees with the experimental result, but is not consistent with the other combinations of phosphorus.

PHOSPHORUS AND IODINE.—When these substances, perfectly dry, are brought together in an exhausted vessel and gently heated, they act violently, evolving heat but no light, and form orange-coloured, red, or black compounds, according to their relative proportions. When one part of phosphorus and about twelve of iodine are fused together, the compound is reddish-brown, very fusible, and appears to be a *sesquiodide of phosphorus* ($p + 1\frac{1}{2} i$), for it is decomposed by water, and resolved into hydriodic and phosphorous acids: it therefore consists of

Phosphorus	1	..	16	..	7·8
Iodine	$1\frac{1}{2}$..	188	..	92·2
Sesquiodide of phosphorus	1		204		100·0

PERIODIDE OF PHOSPHORUS. ($p + 2\frac{1}{2} i$).—When one part of phosphorus is fused with nearly 40 of iodine, a black and less fusible compound results, which is resolved by water into hydriodic and phosphoric acid, and which, therefore, apparently consists of

Phosphorus	1	..	16	..	4·88
Iodine	$2\frac{1}{2}$..	12	..	95·12
Periodide of phosphorus	1		328		100·00

PHOSPHORUS AND BROMINE.—According to M. Balard there are two bromides of phosphorus. When phosphorus and bromine are mixed in a flask filled with carbonic acid, they act intensely upon each other: heat and light are evolved, and a yellow crystalline substance rises to the upper part of the flask, whilst a liquid remains at the bottom. The latter is the *sesquibromide*, it is volatile, and emits pungent fumes when

exposed to air. Water resolves it into hydrobromic and phosphorous acids. The crystalline *perbromide* is converted, by a gentle heat, into a red liquid, and at a higher temperature into red vapour. It emits fumes when exposed to air, and, acted upon by water, forms hydrobromic and phosphoric acid.

Both these bromides are decomposed by chlorine, with the evolution of bromine and the formation of chloride of phosphorus. Iodine, on the contrary, does not decompose them; but bromine decomposes the iodides of phosphorus.

From the action of these bromides on water, there can be little doubt that the former is a *sesquibromide of phosphorus* ($p + 1\frac{1}{2}b$); and that the composition of the *perbromide* corresponds with that of the phosphoric acid and of the perchloride, being ($p + 2\frac{1}{2}b$.)

FLUORIDE OF PHOSPHORUS. ($p + 1\frac{1}{2}f$).—By distilling fluoride of lead or mercury with phosphorus, Davy obtained a fuming liquid, resolved by the action of water into hydrofluoric and phosphorous acids.

PHOSPHORUS AND HYDROGEN; PHOSPHURETTED HYDROGEN; HYDROGURET OF PHOSPHORUS.—Phosphorus may be heated, and even sublimed, in hydrogen gas, without the formation of any definite compound, although, under such circumstances, the gas retains a portion of the vapour of phosphorus, acquiring its peculiar odour, and becoming luminous in the dark when mixed with atmospheric air. When phosphorus is presented to *nascent* hydrogen, two gaseous compounds result. The one inflames spontaneously upon the contact of the atmosphere. This may be procured by heating phosphorus in a solution of caustic potassa; or by acting upon *phosphuret of lime* by dilute hydrochloric acid. In the former case about a quarter of an ounce of phosphorus should be introduced into a small retort, capable of holding about four ounces of water; it should then be completely filled with a moderately-strong solution of potassa, and the beak being placed under the shelf of the pneumatic apparatus, the heat of an Argand lamp carefully applied till it boils: gas will gradually be generated, so as to expel a portion of the alkaline solution, and ultimately to bubble up through the water. Upon coming into contact with the air, the bubbles inflame with a slight explosion; and if the atmosphere is still, each as it bursts produces a beautifully-expanding ring of smoke, in consequence of the sudden formation of phosphoric acid and water. If the retort, in which the gas is generated, contain common air, the first bubbles burn within the vessel, and the retort is frequently broken by the percussion, or by the rush of cold water from the trough, caused by the sudden expansion and subsequent contraction of the air within, an accident prevented by filling the retort with the liquid.

For obtaining this gas by the second process, Dr. Thomson gives the following directions:—Fill a small retort with water, acidulated by hydrochloric acid, and then throw into it a quantity of phosphuret of lime in lumps. Plunge the beak of the retort under water, and place over it an inverted jar filled with that liquid. Phosphuretted hydrogen gas is extricated in considerable quantity, and soon fills the glass jar. Half an ounce of phosphuret of lime yields about 70 cubic inches of this gas. (*Inorg. Chem.*, i. 251.)

This gas was discovered by Gengembre in 1783; it is colourless, has a nauseous odour like onions, a very bitter taste, and inflames when mixed with air, a property which it loses by being kept over water: water takes up about two *per cent.* of this gas, and acquires a bitter taste, and the smell of onions; but the solution has no acid properties like that of sulphuretted hydrogen. When the gas is retained in dry vessels, or over mercury, and carefully excluded from light, it may be kept some time without alteration: but, in the contact of water, and exposed to light, it soon deposits a red film, without changing its volume, and loses the property of spontaneous inflammability. It has been asserted, that in this case the gas deposits half of its phosphorus, and that a definite *subphosphuretted hydrogen* remains; but this statement requires further proof. Houton Labillardière has remarked, that bubbles of phosphuretted hydrogen sent up into a portion of common air standing over mercury, do not inflame when the air is compressed, or when the mercury is at the same level within and without the vessel; but that explosion immediately ensues when the confined air is rarefied by lifting up the jar, so that the column of mercury within may be above that without. When bubbles of phosphuretted hydrogen are sent up into a jar of oxygen, they burn with greatly increased splendour; in chlorine, too, they burn with a beautiful pale blue light, forming hydrochloric acid and perchloride of phosphorus. In a narrow tube it may be mixed with oxygen without exploding, in which case it is deprived of its phosphorus. It burns when thrown up into nitrous oxide.

The specific gravity of this gas, according to Dumas, is 1.761, (*Ann. de Chim. et Phys.*, xxxi. 149,) according to Thomson (*Inorg. Chem.*, i. 252), it is 1.77. When heated with corrosive sublimate, hydrochloric acid gas is formed, equal to three times the volume of the phosphuretted hydrogen decomposed, whence it appears to contain, in the 100 measures, 150 measures of hydrogen; Dumas states the weight of the phosphorus to that of the hydrogen as 15.9 to 1, numbers which closely approximate to 16 and 1, or one equivalent of each of its components.

SESQUIHYDROURET OF PHOSPHORUS; HYDROPHOSPHORIC GAS. ($p + 1\frac{1}{2}h$.)—This compound of phosphorus and hydrogen was discovered by Sir H. Davy, in 1812. It is procured by heating the solid *hydrate of phosphorous acid*, or *hydrophosphorous acid* (p. 489), in a small retort. The gas must be collected over mercury, for water absorbs one-eighth its volume. It is not spontaneously inflammable, but explodes when heated with oxygen. It inflames spontaneously in chlorine. Its smell is less disagreeable than the former.

Both this and the former gas frequently contain free hydrogen, the relative proportion of which may be ascertained by agitation with a cold saturated solution of persulphate of copper, which absorbs the phosphuretted hydrogen, and leaves the pure hydrogen. Dumas infers from the action of perchloride of mercury on this gas, that 100 measures yield 150 of hydrogen. Dr. Turner, on the authority of Dumas and of Buff (*Ann. de Chim. et Phys.*, xli.), considers 100 measures of this variety of phosphuretted hydrogen as constituted of 150 of hydrogen gas, and 25 of the vapour of phosphorus (*Elements of Chem.*), and hence as

		Grains.
150 cubic inches of hydrogen weigh	3.1977
25 " phosphorus vapour	33.5425
100 " phosphuretted hydrogen gas should weigh		36.7402

The calculated density of a gas so constituted should be 1.1853.

It is now generally assumed that the spontaneously inflammable phosphuretted hydrogen derives its peculiarities from the presence of something extraneous, or according to Leverrier (*Ann. C. & P.*, LX. 174), to a gaseous compound of phosphorus and hydrogen ($p+h$), which is decomposed by light. Mr. Graham ascertained that Davy's hydrophosphoric gas was not rendered spontaneously inflammable by the presence of phosphorus vapour, and that the spontaneously inflammable gas was deprived of that property by very minute portions of certain combustible bodies, such as potassium, and the vapour of ether and essential oils; and lastly, that the property was communicated to either gas by the addition of a very minute quantity of nitrous acid vapour, varying from 1-1000th to 1-10,000th of the volume of the gas.

Grotthus has described a liquid compound of phosphorus and hydrogen, analogous probably to the corresponding combination of sulphur, (and, if so, *biphosphuret of hydrogen*,) obtained by boiling phosphorus in an alcoholic solution of potassa. The phosphorus liquifies, and remains fluid when cold; if boiled in water, phosphuretted hydrogen is evolved, but no phosphoric acid is formed, nor is the water decomposed; and phosphorus, which concretes as usual, remains behind. According to Magnus, when phosphuret of potassium is thrown into water, a compound of phosphorus and hydrogen precipitates in the form of a yellow powder. Phosphuretted hydrogen combines with several of the perchlorides, and with the perchloride of tin it forms a compound which is decomposed with the escape of a non-inflammable gas by water, but of a spontaneously inflammable gas by solution of ammonia.

Common phosphorus always yields a trace of hydrogen or of phosphuretted hydrogen, which it evolves when in the act of combining with some of the metals, and Davy found that by acting on fused phosphorus by the voltaic spark, small portions of hydrogen were given off.

PHOSPHORUS AND NITROGEN; PHOSPHURET OF NITROGEN: (see *action of ammonia on chloride of phosphorus*, p. 497.)

AMMONIURET OF PHOSPHORUS.—According to Berzelius, when phosphorus is exposed to ammonia standing over mercury, a *phosphuret of ammonia* is produced, of a dark colour, and pulverulent texture: its properties have not been examined. Bineau could not succeed in obtaining this compound. (*Ann. C. & P.*, LXVII. 229.)

PHOSPHORUS AND SULPHUR; PHOSPHURET OF SULPHUR; SULPHURET OF PHOSPHORUS.—These substances may be united by fusion in an exhausted flask, or under water; in the latter case they combine gradually as soon as the phosphorus is melted, but the heat must be cautiously applied, as the water is sometimes suddenly decomposed with explosive

violence. Mr. Faraday (*Quarterly Journal*, iv. 361) melted 5 parts of sulphur with 7 of phosphorus and agitated the compound in liquid ammonia, by which the reddish-brown colour was removed and a pure fluid of a light-yellow colour, and semitransparent, remained. It retained its fluidity when cooled down to 20° , and was perfectly liquid at 32° . On remaining for some weeks in a bottle of water it deposited crystals of sulphur, and at the temperature of 40° became a crystalline mass, in which the relative proportions of the phosphorus and sulphur appeared to be 8 and 4. This, therefore, was probably a biposphuret of sulphur ($2p + s$), or a compound of

Phosphorus	2	32	66.7
Sulphur	1	16	33.3
<hr/>		<hr/>	<hr/>
Biphosphuret of sulphur	1	48	100.0

This purified compound did not act upon water at common temperatures, nor rapidly even at its boiling-point; hence, Mr. Faraday infers that the rapid action of the compound formed by heat in a tube when in contact with water, results from some combination of oxygen and phosphorus. When the liquid sesquichloride of phosphorus is acted on by sulphuretted hydrogen, hydrochloric acid is evolved, and a yellow substance produced which is a sesquisulphuret of phosphorus. ($p + 1\frac{1}{2}s$.)
—SERULLAS.

§ X. SELENIUM.

THIS rare and singular substance was discovered in 1818 by Professor Berzelius, during an examination of certain substances found in the sulphuric acid manufactured at Gripsholm, in Sweden. (*Ann. de Chim. et Phys.*, ix. 160.) The sulphur used in these works is procured from the iron pyrites of Fahlun, and the acid obtained from it deposits a red matter, which was supposed to contain tellurium, but the peculiarities of which were traced to a distinct and previously unknown substance, to which its discoverer gave the name of *Selenium*, from *Σελήνη*, the moon, in consequence of its having at first been mistaken for the metal Tellurium.

Some difference of opinion exists as to the place which selenium should occupy in chemical arrangements. Berzelius includes it among the metals; but as it is a non-conductor of electricity, and a most imperfect conductor of heat, and as, in other respects, it bears much analogy to sulphur, it is generally placed among the non-metallic combustibles.

Stromeyer and Rose have detected it in several metallic ores from the Hartz mines, and amongst some of the volcanic products of the Lipari islands; and it exists in some of the sulphurets of lead of Fahlun, and in the pyrites of the isle of Anglesey.

Selenium is most readily obtained by the decomposition of *selenic acid*, which may be effected by adding hydrochloric acid to its solution in water, and immersing a plate of zinc in the mixture: a gray or reddish-brown flocculent precipitate of selenium is then deposited. Berzelius, in his *Lehrbuch de Chemie*, has detailed the circuitous process by which he separated selenium from the red sediment of the Gripsholm sulphuric

acid (see also *Ann. of Phil.*, xiv. 403); and M. Lewenau has described some important improvements in the modes of obtaining it in a pure state. (*Ann. of Phil.*, N. S., viii. 104.)

To extract selenium from the native sulphuret, Magnus proposes to mix it with eight times its weight of peroxide of manganese, and to expose the mixture to a low red heat in a glass retort, the beak of which dips into water. The sulphur, oxidized at the expense of the manganese, escapes in the form of sulphurous acid, while the selenium either sublimes as such or in the state of selenious acid: should any of the latter go over into the water it would there be reduced by the sulphurous acid. (TURNER, *Elem. of Chem.*)

Selenium, when cooled after fusion, has a reddish-brown colour, and dim metallic lustre; its fracture is of a lead-gray colour. Its specific gravity is 4.32. Specific heat = 0.0837. (REGNAULT.) Obtained from its solutions by precipitation upon zinc, it is red, but becomes black when boiled in water. A dilute solution of selenic acid mixed with sulphurous acid, and exposed to light, becomes covered with a film of reduced selenium of a gold colour. When fused, and very slowly cooled, its surface is gray and granular, without lustre: and its fracture dull, like that of metallic cobalt. It is brittle, soft, and easily reduced to powder. Under certain circumstances, it assumes a prismatic crystalline texture, but not very distinct. In thin layers it is transparent, transmitting red rays; it is softened by heat, becoming semifluid at 212° , and perfectly fusing at a temperature somewhat higher; it remains for some time soft on cooling, and may be drawn out into filaments like sealing-wax, which are of a gray metallic lustre by reflected light, but by transmitted light of a clear ruby-red. Heated in a tube or small retort nearly to redness, or about 650° , it boils, and is converted into a yellow vapour of a deeper colour than chlorine, which condenses into black drops that run together like quicksilver. Heated in the open air it rises in vapour, which may be condensed into a red powder. It is characterized by tinging the flame of the blowpipe of a light blue colour, and by exhaling, when strongly heated, a peculiar and highly diffusible odour of decayed horseradish.

SELENIUM AND OXYGEN.—These bodies appear to unite in three proportions, forming an oxide and two acids.

SELENIOUS OXIDE; OXIDE OF SELENIUM ($Se + O$), is formed by heating selenium in a limited quantity of atmospheric air, and washing the product to separate a portion of acid which is at the same time formed. The characters of this compound have not been accurately examined, nor has its composition been ascertained: it is sparingly soluble in water, and passed through alkaline solutions, imparts to them its peculiar odour, but is not absorbed: it does not redden litmus. It appears to be the cause of the peculiar odour emitted during the oxidation of selenium. It probably consists of

Selenium . . .	1	40	88.3
Oxygen . . .	1	8	16.7
	<hr/>	<hr/>	<hr/>
	1	48	100.0

SELENIOUS ACID. ($Se + 2O$) or Se' .—When a current of oxygen gas is passed over selenium, heated to its boiling-point, it burns with a pale bluish-green flame, and this acid sublimes and condenses in long brilliant prismatic crystals, provided the vessel into which it is received is cold and capacious; otherwise, the sublimate is semifused and semitransparent: this is dry selenious acid: it loses its transparency by exposure to air, and rapidly absorbs water. Exposed to heat, the water separates again before the acid rises in vapour. Selenious acid may also be obtained by digesting selenium in nitric or nitrohydrochloric acid till entirely dissolved, and then evaporating to dryness. Its taste is sour and hot; its odour, when sublimed, acid, but not like that of the oxide. It is very soluble in warm water, and the solution furnishes crystals of hydrated acid. It also dissolves in alcohol, and the solution furnishes, on distillation, a liquid of an ethereal odour. If this alcoholic solution be mixed with sulphuric acid, and then distilled, the product has an odour so insupportable, that Berzelius was unable to proceed in its examination.

The selenious acid and its salts may be decomposed by mixture with solution of sulphite of ammonia and the addition of an acid. Sulphurous acid is liberated, and the selenium is slowly reduced, the solution first acquiring a yellow colour, and in the course of some hours depositing red flocculi of selenium: this effect is accelerated by a boiling heat. This acid forms precipitates in the solutions of silver and of lead; its neutral salts with alkaline bases convert vegetable blues to green, and redden turmeric. It combines also in two and four proportionals with certain bases, so that it forms *selenites*, *biselenites*, and *quadriselenites*. It forms very few subsalts.

The proportion of oxygen in this acid is, to that contained in the bases to which it unites to form neutral salts, as two to one; so that it may be considered as a compound of

						Berzelius.
Selenium	.	.	1	.	40	71.43
Oxygen	.	.	2	.	16	28.57
<hr/>						<hr/>
Selenious acid			1		56.	100.00
						100.000

SELENIC ACID. ($Se + 3O$) or Se' .—This acid was first described by MM. Mitscherlich and Nitzsch. (*Ann. de Chim. et Phys.*, vol. xxxvi., p. 100.) It is obtained by fusing selenium, or selenious acid, or any of its salts, or a metallic seleniuret, with nitrate of potassa or of soda: seleniuret of lead, as the most common ore containing it, has generally been used: it is to be digested in hydrochloric acid, to separate carbonates, and the residue mixed with its weight of nitrate of soda, and gradually thrown into a red-hot crucible; the fused mass is then well washed in hot water, which dissolves the alkaline seleniate and the nitrate: this solution, quickly boiled down, deposits seleniate of soda, and this being separated, the nitrate crystallizes on cooling; the mother-liquor again boiled deposits more of the seleniate, and in this way the salts may be separated; for the seleniate, like sulphate of soda, is more soluble in water at about 90° than at 212° . The seleniate of soda thus obtained is not quite pure; if it be mixed with hydrochlorate of ammonia and heated,

nitrogen and water are evolved, selenium sublimes, and chloride of sodium is formed: the selenium is now pure, and may be converted by nitric or nitrohydrochloric acid into selenious acid, neutralized with soda, and this converted into seleniate by fusion with nitrate of soda, solution, and crystallization, as before. The solution of this pure seleniate may now be decomposed by nitrate of lead; the insoluble seleniate of lead is well washed and diffused through water, into which a current of sulphuretted hydrogen is passed to precipitate the lead: the liquid is boiled, to evaporate excess of sulphuretted hydrogen, and is now dilute selenic acid. Its purity, as respects fixed bodies, is determined by its perfect volatility; if sulphuric acid be present, it may be ascertained by boiling a portion with hydrochloric acid, which produces selenious acid, and then testing by chloride of barium.

Selenic acid is a colourless liquid, which may be heated to about 536° without decomposition; it is partially changed at higher temperatures; and at 554° , is rapidly resolved into selenious acid and oxygen. When concentrated, by exposure to a temperature of about 329° , it acquires a specific gravity of 2.524; at 513° , it is 2.6: it may be rendered somewhat denser by evaporation at higher temperatures; but in that case a portion of selenious acid is formed in it; and it is impossible to expel the whole of its water without decomposition: it is unknown in its anhydrous state.

Selenic acid has a strong attraction for water, and evolves much heat when mixed with it; sulphuretted hydrogen does not decompose it, and hence that gas may be used to decompose some of the metallic seleniates. When boiled with hydrochloric acid, selenious acid and chlorine are produced, so that the selenio-hydrochloric acid dissolves gold upon the same principle as the nitro-hydrochloric. It dissolves zinc and iron with the evolution of hydrogen; and copper, with the production of selenious acid; it also dissolves gold, but not platinum; sulphurous acid, which decomposes selenious acid, has no action on selenic acid; so that to decompose selenic acid in this way, it must first be boiled with hydrochloric acid, which converts it into selenious acid, and the sulphurous acid, or a sulphite, then effects the separation of selenium. The affinity of selenic acid for bases is little inferior to sulphuric acid, for seleniate of baryta is not completely decomposed by sulphuric acid.

From the resemblance, in crystalline form, of the seleniates to the sulphates, Mitscherlich inferred that the proportion of oxygen in selenic acid should correspond to that in sulphuric acid; that it should be to the base as three to one; and to that in the selenious acid as three to two. These views were confirmed by experiment; the selenic acid, therefore, consists of

					Mitscherlich.	
Selenium	. 1	. . 40	. . 62.5	. . 61.4		
Oxygen	. 3	. . 24	. . 37.5	. . 38.6		
<hr/>						
Selenic acid	1	64	100.0	100.0,		

SELENIUM AND CHLORINE.—When chlorine is passed over selenium, it is absorbed with the production of heat, and a brown liquid *chloride of selenium* ($Se + 2C$), results, not very volatile, heavier than water, and

gradually resolved by the action of water into hydrochloric and selenious acids.

Exposed to excess of chlorine, this deutochloride absorbs an additional quantity, and becomes converted into a white solid *perchloride* ($se + 3c$), which volatilizes when heated, and condenses in the form of delicate crystals. It dissolves with the evolution of heat in water, producing a colourless sour solution, which probably contains muriatic and selenic acids.

SELENIUM AND BROMINE.—These substances readily combine with the evolution of heat into a reddish-brown fuming compound, having the odour of chloride of sulphur: it is converted by the action of water into hydrobromic and selenious acids. (SERULLAS, *Ann. de Ch. et Ph.*, xxxv. 349.) It is, therefore, probably a compound of 1 atom of selenium and 2 of bromine. ($se + 2b$.)

The *iodide* and *fluoride* of selenium appear not to have been examined.

SELENIUM AND HYDROGEN; SELENIURETTED HYDROGEN; HYDROSELENIC ACID. ($se + h$) or *hse*.—This gaseous compound may most easily be obtained by the action of hydrochloric acid upon seleniuret of potassium or of iron. It is colourless, and readily dissolves in water, forming a solution at first colourless, but after a time acquiring a reddish hue: the solution smells and tastes somewhat like that of sulphuretted hydrogen; it reddens litmus, and permanently tinges the skin of a reddish-brown. Nitric acid dropped into it occasions no change, and the gas does not readily escape from the water; but, when exposed to air, the solution gradually reddens, and deposits selenium. It occasions precipitates in all solutions of neutral metallic salts, which are black or dark-brown, with the exception of those from zinc, manganese, and cerium, which are flesh-coloured.

Seleniuretted hydrogen is easily decomposed by the joint action of air and water; it is absorbed by moist substances, and soon communicates to them a red colour. The selenium is thus remarkably deposited throughout the texture of organic bodies. A piece of moist paper is penetrated by the red colour. Moist wood, and even a thin piece of caoutchouc, became in the same way red throughout. It exerts a dangerous action upon the trachea and organs of respiration; it inflames the eyes, and painfully stimulates the nasal membrane, destroying for some hours the sense of smell. Berzelius states that in the first experiments which he made upon this gas, he let up into his nostrils a bubble about the size of a pea. "It deprived me so completely of the sense of smell, that I could apply a bottle of concentrated ammonia to my nose without perceiving any odour. After five or six hours I began to recover the sense of smell, but a severe catarrh remained for about fifteen days." On another occasion, a little of the gas accidentally escaped; it produced a sharp sensation in the nose, red eyes, and a dry and painful cough, at length succeeded by expectoration tasting like the vapour from a boiling solution of corrosive sublimate. "These symptoms were removed by a blister to my chest. The quantity of seleniuretted hydrogen gas which on each of those occasions entered into my organs of

respiration, was much smaller than would have been required of any other inorganic substance whatever to produce similar effects." (*Ann. of Phil.*, xiv. 101.) Dr. Prout, in his *Bridgewater Treatise*, quotes the above passage, to show how small a quantity of foreign matter may, when diffused in the atmosphere, produce powerful effects upon the human system, and suggests the possibility of some such cause, as the origin of influenza, and some other epidemic disorders.

The specific gravity of seleniuretted hydrogen has not been ascertained, but from its analysis (BERZELIUS, *Ann. de Ch. et Ph.*, ix. 335), it appears to consist of

				Berzelius.	
Selenium	1	. . 40	. . 97.56	. . 97.4
Hydrogen	1	. . 1	. . 2.44	. . 2.6
<hr/>				<hr/>	
Seleniuretted hydrogen		1	41	100.00	100.0

SELENIUM AND NITROGEN have no mutual action, nor does selenium absorb ammonia; but when seleniuret of calcium and hydrochlorate of ammonia are mixed and distilled, a red fluid is obtained, of an hepatic odour, and decomposed by exposure to air, exhaling ammonia, and leaving selenium.

SELENIUM AND SULPHUR; SULPHURET OF SELENIUM.—Sulphur and selenium may be mixed by fusion in all proportions. An addition of about one per cent. only of sulphur renders selenium more red, fusible, and transparent when cold. A true *sulphuret of selenium* may be obtained by passing sulphuretted hydrogen into a solution of selenious acid: the fluid becomes turbid, and acquires a fine yellow colour, but the precipitate is long in separating, unless a little hydrochloric acid be added: when warmed, it acquires a red colour and viscid texture, and may be distilled, without decomposition, at high temperatures. It is slowly acted upon by nitric acid, but nitro-hydrochloric acid easily decomposes it; it is soluble in the caustic fixed alkalis, and in their hydro-sulphurets, forming yellow solutions, from which acids precipitate it. Burned in the air, it at first exhales a sulphurous odour, but afterwards the smell of horseradish prevails. It is a *bisulphuret of selenium* ($se + 2s$), for it consists, according to Berzelius, of

				Berzelius.	
Selenium	1	. . 40	. . 55.6	. . 55.21
Sulphur	2	. . 32	. . 44.4	. . 44.79
<hr/>				<hr/>	
Bisulphuret of selenium		1	72	100.0	100.00

SELENIUM AND PHOSPHORUS; PHOSPHURET OF SELENIUM.—Dropped into melted phosphorus, selenium forms a red compound, apparently soluble in all proportions in the fused phosphorus. When phosphorus is saturated with selenium, an easily-fusible compound results, which, on cooling, acquires a brown lustre and vitreous fracture. When this *phosphuret of selenium* is digested in water, a small portion of the phosphorus is oxidized, and the water acquires the odour of seleniuretted hydrogen, and deposits selenium when exposed to the air. The compound is dissolved when boiled in caustic potassa, and the solution contains phosphate and hydroseleniuret of potassa. (BERZELIUS, *Ann. de Ch. et Ph.*, ix. 238.)

§ XI. CARBON.

THE purest form of this elementary substance is the *diamond*, a mineral body first discovered in Asia, in the provinces of Golconda and Visapour, in Bengal, and in the island of Borneo. About the year 1720, diamonds were first found in the district of Serra Dofrio, in Brazil, and from this locality the European market is now chiefly supplied. They occur in detached crystals in alluvial soil; though it appears probable, from a specimen described by Mr. Heuland (*Geol. Trans.*, 2nd series, i. 419), that in Brazil the real matrix is an iron-stone which forms beds resting on primary chlorite slate. According to Mr. Voysey, the diamonds of the Nalla Malla Mountains, in Hindostan, are found in a species of pudding-stone or breccia, composed of fragments of jasper, quartz, and calcedony. (*Phil Mag.*, 2nd series, i. 147.) The primitive form of the diamond is the regular octoëdron, each triangular facet of which is sometimes replaced by six secondary triangles, bounded by curved lines; so that the crystal becomes spheroidal, and presents forty-eight facets. Diamonds, with twelve and twenty-four facets, are not uncommon. (JAMESON'S *Mineralogy*, 2nd edit., vol. i. p. 1.) The diamond has been found nearly of all colours: those which are colourless are most esteemed; then those of a decided red, blue, or green tint. Black diamonds are extremely rare. Those which are slightly brown, or tinged only with other colours, are least valuable.

The fracture of the diamond is foliated, its laminae being parallel to the sides of a regular octoëdron. It is somewhat brittle but very hard; its specific gravity varies from 3.4 to 3.6, it is most commonly 3.52. It is a non-conductor of electricity, frequently phosphorescent (p. 217), and has a very high refractive power in regard to light, as compared with its density (p. 192). It is not acted upon by any acid or alkali.

The art of cutting and polishing diamonds, though probably of remote antiquity in Asia, was first introduced into Europe in 1456, by Louis Berghen, of Bruges, who accidentally discovered, that, by rubbing two diamonds together, a new facet was produced. The particular process of forming the rough gems into *brilliant*s and *rose diamonds* has been described at length by Jeffries. (*On Diamonds and Pearls*, 3rd edit., London, 1800.) By either of these processes, but especially by the former, so much is cut away, that the weight of the polished gem does not exceed half that of the rough stone; so that the value of a brilliant-cut diamond is esteemed equal to that of a similar rough diamond of twice the weight, exclusive of the cost of workmanship. The weight, and therefore the value of diamonds is estimated in *carats*, 150 of which are about equal to one ounce troy, or 480 grains. They are divided into halves, quarters, or carat grains, eighth, sixteenth, and thirty-second parts.

The difference of value between one diamond and another of equal merit, is, generally speaking, as the squares of their respective weights: thus, the value of three diamonds, of one, two, and three carats' weight respectively, is as one, four, and nine. The average price of rough

diamonds is estimated by Jeffries at 2*l.* per carat; and, consequently, when wrought, the cost of the first carat, exclusive of workmanship, will be 8*l.*, which is the value of a rough diamond of two carats.

		£.
A wrought diamond of 3 carats is worth		72
" 4 ditto		126
" 5 ditto		200
" 10 ditto		800
" 20 ditto		3,200
" 30 ditto		7,200
" 40 ditto		12,800
" 50 ditto		20,000
" 60 ditto		28,800
" 100 ditto		80,000

This mode of valuation, however, only applies to small diamonds, in consequence of the difficulty of finding purchasers for the larger ones.

The largest known diamond is probably that mentioned by Tavernier, in the possession of the Great Mogul: its size is about that of half a hen's egg; it is cut in the rose form, and when rough, is said to have weighed 900 carats: it was found in Golconda about the year 1550. Among the crown-jewels of Russia is a diamond weighing 195 carats: it is the size of a small pigeon's egg, and was formerly the eye of a Brahminical idol, whence it was purloined by a French soldier; it passed through several hands, and was ultimately purchased by the Empress Catherine, for the sum of 90,000*l.* in ready money, and an annuity of 4000*l.* Perhaps the most perfect and beautiful diamond hitherto found, is a brilliant brought from India by an English gentleman of the name of Pitt, who sold it to the Regent Duke of Orléans, by whom it was placed among the crown jewels of France: it weighs rather more than 136 carats, and was purchased for 100,000*l.* In the year 1828, a collection of diamonds of extraordinary size and beauty was in the possession of Messrs. Rundell, Bridge, and Co., of London: the suite consisted of eight, of various shapes and sizes, the smallest weighing 55 grains, and the largest 151 grains: with one exception they were all brilliant cut.

The principal use of the diamond is in jewellery, but it is also importantly applicable in some of the arts; in consequence of its extreme hardness it is employed for the pivot-holes in delicate watch and clock-work, and it has been used to form the holes through which extremely fine wires are drawn: it also furnishes the only convenient tool for cutting glass; for this purpose the edge of one of the small curvilinear crystals is used, for the edges of the crystals formed by flat plates only scratch, without producing that peculiar fissure by which the glass can be smoothly split. Microscopic lenses have also been formed of diamond.

CHARCOAL.—This is another well-known form of *carbon*: it is obtained in abundance by the destructive distillation of various organic products, and its characters and properties vary with its source. It may be prepared by heating pieces of wood in a close vessel, or in a crucible covered with sand, to redness, and keeping them in that state for about an hour, or till all volatile matters are expelled. They are thus converted into a black brittle porous substance, which appears to be essentially the same, from whatever kind of wood it has been procured.

Common charcoal, employed as fuel, is usually made of oak, chestnut, elm, beech, or ash wood, the white and resinous woods being seldom used. Young wood affords a better charcoal than large timber, which is also too valuable to be thus employed. The billets are formed into a conical pile, which, being covered with earth or clay, is suffered to burn with a limited access of atmospheric air, by which its complete combustion, or reduction to ashes, is prevented. (See URE's *Dict. of Arts*, Art. CHARCOAL.)

Another, and a more perfect mode of preparing charcoal, consists in submitting the wood to a red heat in a kind of distillatory apparatus consisting of cast-iron cylinders, from which issue one or more tubes for the escape of gaseous matters and vapours. The makers of gunpowder particularly prefer this process. (A plate of this apparatus is given in PARKES *Chemical Essays*.)

The quantity of charcoal obtained from different kinds of wood is liable to much variation. The following table drawn up from the experiments of Allen and Pepys (*Phil. Trans.*, 1807), and of Griffiths (*Quar. Jour.*, xvi. 264), shows the produce of charcoal from 1000 parts of several varieties of dense and light woods.

Ebony	305	Box	202
Botany Bay-wood	281	Fir	181
Brazil-wood	260	Lignum-vitæ	175
Eveas-wood	225	Oak	174
King-wood	220	Mahogany	157
Tulip-wood	208	Beech	150
Satin-wood	207		

Charcoal is a black, insoluble, inodorous, insipid, brittle, substance; an excellent conductor of electricity, but a bad conductor of heat; unchanged by the combined action of air and moisture at common temperatures, and easily combustible in oxygen gas. Its specific heat, as estimated by Regnault, is 0.24111; the average, as given by Dulong and Petit, is 0.25. When pure it is perfectly infusible at all known temperatures; in the cases in which it was supposed to have been fused, some impurities apparently have existed in the charcoal employed; upon this subject a series of experiments have been published by Silliman (*Quarterly Journ.*, xvi. 157). Under common circumstances of ignition it does not appear to volatilize, but from the experiments of Leplay and Laurent (*Ann. C. et P.*, lxxv. 417), it seems not improbable that in the process of steel-making the penetration of iron by carbon may be partly due to its volatility. It is capable of destroying the smell and taste of a variety of vegetable and animal substances, and of abstracting certain substances dissolved in fluids. (LOWITZ, CRELL's *Annals*, ii. 165.) The use of charring piles; of throwing charcoal into putrid water; of wrapping it in clothes that have acquired a bad smell; of adding it to port wine, with a view of making it tawny, depends upon the above properties. M. Bussy has published some interesting observations on the discolouring power of charcoal, in the *Journal de Pharmacie* for June, 1822, of which an abstract will be found in the *Quarterly Journal*, xiii. 406. It appears from his experiments, that certain physical conditions are requisite for the manifestation of this property, especially porosity and minute division,

and that it is not possessed by any hard and brilliant charcoal even when finely powdered. Upon this principle, he accounts for the superior efficacy of the charcoal obtained by burning animal substances, over that of vegetables, in the destruction of colour. According to Payen, animal charcoal, boiled with lime-water, deprives it entirely of lime, an effect not produced by lamp-black or vegetable charcoal. (*Quarterly Journal*, xv. 384.) Well-burned charcoal shaken with water contaminated by sulphuretted hydrogen, entirely deprives it of that gas, so that when filtered it is not only inodorous, but is not discoloured by solution of lead.

Newly-made charcoal has the property of absorbing certain quantities of the different gases. Upon this subject the experiments of M. Theodore de Saussure are the most recent. (THOMSON'S *Annals*, vol. vi.) The charcoal was heated red-hot, then suffered to cool under mercury, and introduced into the gas. The following are the volumes of different gases absorbed by a volume of charcoal = 1.

Ammonia	90	Bicarburetted hydrogen	35
Hydrochloric acid	85	Carbonic oxide	9.42
Sulphurous acid	65	Oxygen	9.25
Sulphuretted hydrogen	55	Nitrogen	7.5
Nitrous oxide	40	Carburetted hydrogen	5
Carbonic acid	35	Hydrogen	1.75

The absorption was always at its maximum at the end of twenty-four hours, not being increased by retaining the charcoal in the gas. When charcoal, already saturated with any one gas, is put into another, it gives out a portion of the gas already absorbed, and takes up a portion of the new gas. It would also appear that this absorptive quality partly depends upon the mechanical texture of the charcoal, and consequently will vary in the different woods; for, by exposing the charcoal of different woods to air, Allen and Pepys found that they increased very differently in weight.

By a week's exposure, charcoal from

Lignum-vitæ gained	9.6 per cent.	Beech	16.3 per cent.
Fir	13.0 "	Oak	16.5 "
Box	14.0 "	Mahogany	18.0 "

The matter absorbed in these cases consisted principally of aqueous vapour, which is very greedily imbibed by newly-made charcoal.

According to Vogel, when recently-ignited charcoal, which has been cooled under mercury, is put into a jar of atmospheric air, it absorbs the oxygen of the air to a much greater extent than the nitrogen. (SCHWEIGER'S *Journal*, iv.) A piece of well-burned charcoal cooled under mercury and then introduced into a mixture of oxygen and sulphuretted hydrogen gases rapidly absorbed them, and then became ignited and caused explosion. (A. TAYLOR.)

WOOD CHARCOAL generally contains about one-fiftieth of its weight of alkaline and earthy salts, which remain in the form of *ash*, after its combustion, but the quantity and quality of this ash vary considerably in different trees and plants.

ANIMAL CHARCOAL, obtained by the carbonization of animal substances, such as muscle, horn, or hoof, resembles the former in its general characters, but instead of retaining the form of the matter from which it is produced, as is the case with the generality of vegetable charcoal, it appears as if it had undergone fusion, and often has a peculiar lustre and sponginess. The residuary charcoal, obtained by the distillation of bone, is called *ivory-black* in commerce, and is very impure, being mixed with the phosphate of lime and other salts contained in the earthy part of the bone, so that for many purposes it requires to be freed from its earthy salts by digesting it in dilute hydrochloric acid, and then washing and drying it; but by this process its discolouring power is greatly impaired. Some of the peculiarities of animal charcoal as regards the destruction of odours and colour have already been mentioned, and have been referred to its peculiar texture, rather than to any peculiarity of composition, charcoal being essentially the same, under all its various forms. When vegetable matter, for instance, mixed with earthy substances are charred, they yield a product the properties of which resemble those of animal charcoal: thus a mixture of 100 parts of thin pipe-clay, 20 of tar, and 500 of powdered coal dried and calcined, gave a charcoal of great decolourizing power. Of the different kinds of charcoal used for decolouration, bone charcoal, or ivory black, is most feeble, although it is far superior to the best wood charcoal. The following table shows the efficiency of several varieties of these charcoals compared with ivory-black. Column I. represents 1 gramme (or 15·4 grains) of the different kinds of charcoal experimented on. Column II. shows the quantity of test indigo liquor (in grammes) decoloured by each gramme of the respective charcoals; this indigo liquor contained one-thousandth of indigo, so that each gramme of the decoloured liquor represents a thousandth of a gramme of indigo absorbed by the charcoal. Column III. shows the relative decolouration of a solution of 1 part of raw sugar in 20 of water, also in grammes. Column IV. shows the relative decolouration of the indigo, and Column V. that of the brown syrup, in reference to the effect of ivory-black.

I.	II.	III.	IV.	V.
1. Common bone charcoal, or ivory-black	32	9	1·00	1·00
2. Oil charred with phosphate of lime	64	17	2·00	1·90
3. Bone charcoal washed with hydrochloric acid	60	15	1·87	1·60
4. No. 3 calcined with carbonate of potassa	1450	180	45·00	20·00
5. Calcined lamp black	128	30	4·00	3·30
6. No. 5 calcined with carbonate of potassa	550	90	15·20	10·60
7. Charcoal of carbonate of soda decomposed by } phosphorus	380	80	12·00	8·80
8. Charcoal of acetate of potassa	180	40	5·60	4·40
9. Starch calcined with carbonate of potassa	340	80	10·60	8·80
10. Albumen or gelatin calcined with carbonate of } potassa	1115	140	35·00	15·50
11. Blood charred with phosphate of lime	380	90	12·00	10·00
12. Blood charred with carbonate of lime	570	100	18·00	11·00
13. Blood charred with carbonate of potassa	1600	180	50·00	20·00

LAMP-BLACK is prepared principally by the combustion of refuse and residuary resin, left by the distillation of turpentine. It is burned in a furnace, so constructed that the dense smoke arising from it may pass into

chambers hung with old sacking, where the *soot* is deposited, and from time to time swept off, and sold without any further preparation. (AIKIN'S *Dictionary*, Art. *Charcoal*. DUMAS, *Chim. App. aux Arts*.) When lamp-black has been heated red-hot, it may be regarded as a very pure form of charcoal, for it burns entirely away, and leaves no residuary ash: when, however, the products of its combustion are closely examined, it is found to yield traces of water, and therefore probably contains hydrogen in chemical combination. A substance analogous to lamp-black is obtained by passing the vapour of certain oils, and of hydrocarbonous compounds, through red-hot tubes; at that high temperature they are more or less perfectly decomposed, and let fall a quantity of very impalpable charcoal, in which, however, as in lamp-black, traces of hydrogen may be detected. One of the principal uses of lamp-black is in the manufacture of printer's-ink. For this purpose it has lately been obtained by the combustion of purified coal-tar. (URE'S *Dict. of Arts*, Art. *Black*.)

COAL-GAS CHARCOAL.—A very singular form of charcoal is occasionally deposited in coal-gas retorts, and in the tubes connected with them, resulting from the decomposition of the first products of the distillation of coal. It has a gray colour, and often exhibits a laminated texture; its streak is black, and it breaks with an earthy fracture: its specific gravity is about 1·8. It sometimes happens that the gas escapes through some crack in the retort, in which case a peculiar carbonaceous deposit forms upon the surrounding brick-work, of a stalactitic character, an iron-gray colour, and considerable lustre; it does not easily burn, nor does it soil the fingers; and some specimens, as far as mere appearance goes, might be considered as metallic. Its specific gravity is about 1·75. Some years ago, Mr. Charles Macintosh, of Glasgow, made steel by passing coal-gas over ignited iron, placed in an air-tight iron chest: in this process much carbon was deposited in various states, but some of it assumed the remarkable form of capillary filaments, and tufts of a metallic lustre; they were very difficult of combustion, but when deflagrated with nitre yielded no trace of iron, and were apparently pure carbon. All these forms of carbon were conductors of electricity. (COLQUHOUN, *Ann. of Phil.*, N.S., xii. 50.)

PLUMBAGO. GRAPHITE. BLACK LEAD.—This substance must be considered as one of the forms of carbon. It is well known in the manufacture of pencils, for which purpose it is almost exclusively obtained from the mine of Borrowdale, at the west end of Derwent Lake, in Cumberland, where it was first wrought during the reign of Elizabeth. In a less pure state it is not an uncommon mineral, occurring in detached masses generally in primitive rocks. It is of an iron-gray colour, metallic lustre, and soft and greasy to the touch: its specific gravity varies from 1·9 to 2·3; it occasionally occurs crystallized in hexangular plates; it conducts electricity, is infusible, and very difficult of combustion: when burned in a stream of oxygen gas, it leaves a small quantity of yellow ash, composed chiefly of oxide of iron, but varying in quantity in different specimens. According to Vanuxen (SILLIMAN'S *Jour.*, x. 105), the following are the components of three varieties of this mineral; the two first are the pure

and impure varieties from Borrowdale, and the third a pure specimen from Bustletown, Pennsylvania.

	1.	2.	3.
Carbon	88.37	61.27	95.4
Water	1.23	5.33	0.6
Silica	5.10	10.10	2.6
Alumina	1.00	3.20	0.0
Oxides of iron and manganese .	3.60	20.00	1.4
	<hr/> 99.30	<hr/> 99.90	<hr/> 100.0

Schrader analyzed the ashes remaining after the combustion of 200 grains of English and 200 grains of Spanish plumbago, with the following results. (*Ann. of Phil.*, i. 294.)

	Borrowdale.	Spanish.
Protoxide of iron	11.6	14.2
Silica	7.0	3.0
Alumina	4.6	2.4
Oxide of copper	0.0	1.0
Titanic acid	6.3	3.1
	<hr/> 29.5	<hr/> 23.7

It seems, probable, therefore, that in plumbago the oxide of iron is in combination with titanic acid and silica, and not with the carbon so as to constitute a *carburet of iron*. Some specimens, indeed, as those from Barreros in Brazil, scarcely contain a trace of iron.

ANTHRACITE. MINERAL CHARCOAL. GLANCE-COAL.—The *culm* of Wales, and the *Kilkenny-coal* of Ireland, are species of this mineral. It much resembles common coal in appearance, but is difficult of combustion, and burns without flame, smell, or smoke, and leaves very little ash. Its specific gravity is about 1.4.

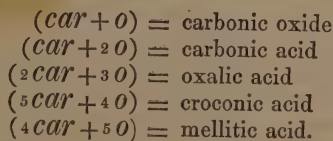
COKE is the carbonaceous residue of the distillation of pit-coal; it has a porous texture, and more or less lustre, frequently appearing metallic; in small fragments it is very difficult of combustion in the flame of a candle, but when employed in large masses as fuel, it produces an intense and steady heat. It varies extremely in purity, but when carefully prepared from the purest varieties of coal, it leaves very little residue after combustion.

Such are the principal varieties of carbon: the diamond appears to be this element in its pure form, for it burns away without residue, and affords no appreciable traces of any foreign matter: the other forms of carbon, on the contrary, yield indications of extraneous substances, such as hydrogen, or metals, or their oxides. They are all infusible, and the porous varieties are very bad conductors of heat: with the exception of the diamond, they conduct electricity, but some of them more perfectly than others, and plumbago and very dense and well-burned wood-charcoal almost rival some of the metals in this respect; this circumstance, and the strong lustre of some of the species of charcoal, seem almost to justify Döbereiner in placing it among the metals under the name of *Carbonium*.

CARBON AND OXYGEN.—Though these substances possess for each other a very powerful affinity, they do not combine at common tempera-

tures: to this remark, however, there are, perhaps, some exceptions, and it appears that certain forms of carbon may exist, which produce carbonic acid whenever they come into contact with oxygen; these are, probably, peculiar to organic combinations.

There are three definite compounds of carbon and oxygen; namely, the *carbonic oxide*, *carbonic acid*, and *oxalic acid*; the oxalic acid is exclusively derived from organic products, and, in all its chemical relations, is so connected with the *vegetable acids*, that I shall refer it and its combinations to that class of bodies: Döbereiner has termed it the *carbonous acid*; but, as Berzelius observes, there is not that analogy between the oxalic and carbonic acids that exists in reference to the sulphurous, and phosphorous, and sulphuric, and phosphoric acids, and which would justify such nomenclature. L. Gmelin includes *croconic acid* among the combinations of carbon and oxygen: it is produced during the action of charcoal upon carbonate of potassa at high temperatures, (see Potassium,) and consists according to Gmelin of 5 atoms of carbon and 4 of oxygen, if supposed anhydrous. The *mellitic acid* in its anhydrous state is also placed by Liebig and Wöhler among the acids of carbon, containing 4 atoms of carbon and 5 of oxygen. We shall here limit ourselves to the history of carbonic oxide and carbonic acid; but assuming the existence of anhydrous oxalic, croconic, and mellitic acids, we have the following formulæ of the combinations of carbon and oxygen:—



CARBONIC OXIDE. GASEOUS OXIDE OF CARBON. ($car + o$) CO or C̄. This gas, which was discovered by Dr. Priestley (*Obs. on Air*, i. 298), is usually obtained by subjecting *carbonic acid* to the action of substances which abstract a portion of its oxygen. Upon this principle it is produced by heating in an iron retort, a mixture of chalk and charcoal; or of equal weights of chalk and iron or zinc filings. It is also obtained by heating a mixture of equal parts of oxide of zinc and charcoal; but the mixture that affords it most pure is equal parts of carbonate of baryta and clean iron-filings; these should be introduced into a small earthen retort, so as nearly to fill it, and exposed to a red heat: the first portion of gas being rejected as mixed with the air of the retort, it may afterwards be collected quite pure: it should, however, be well washed with lime-water, and may afterwards be preserved over water. Carbonic oxide may also be obtained by gently heating oxalic acid with five or six times its weight of sulphuric acid; the mixture effervesces in consequence of the evolution of equal volumes of carbonic oxide and carbonic acid gas; the latter may be abstracted by a caustic alkaline solution, and pure carbonic oxide gas remains. (DUMAS, *Edinburgh Journal of Science*, vi. 350.) In this case the evolution of carbonic oxide is caused by the abstraction of water from oxalic acid which contains in its anhydrous state the elements of 1 atom of carbonic oxide and 1 atom of carbonic acid, but these can only exist

as oxalic acid when in union with water, or with a base, anhydrous oxalic acid not having been isolated. It not unfrequently happens that carbonic oxide is formed by the combustion of carbon when the supply of oxygen is inadequate to the production of carbonic acid: hence the lambent blue flame which sometimes plays upon a coke or charcoal fire, or is seen to issue from certain furnaces.

The nature of carbonic oxide was first made known by Mr. Cruickshank, of Woolwich, in 1802 (NICHOLSON'S 4to. *Journal*, v.); and about the same time it was examined by Clement and Desormes. (*Ann. de Chim.*, xxxix. 26.)

The specific gravity of this gas compared to hydrogen is as 14 to 1; and to atmospheric air as 0.972 to 1000; 100 cubical inches weighing 30.2 grains. (At the temperature of 32° 100 cubic inches weigh 31.8790 grains. THOMSON.) It is fatal to animals, and produces giddiness and fainting when respired mixed with atmospheric air. (*Phil. Mag.*, xliii. 367.) When breathed pure it almost immediately induces profound coma. It extinguishes flame, and burns with a peculiar blue light, when mixed with, or exposed to, atmospheric air. Sir H. Davy found that the temperature of an iron wire heated to dull redness, was sufficient to inflame it. It has no taste and little odour, it does not affect vegetable colours, occasions no precipitate in lime water, and is very sparingly absorbed by water which has been deprived of air. When burned under a dry bell-glass of air or oxygen, no moisture whatever is deposited, showing that it contains no hydrogen.

Carbonic oxide suffers no change by being passed and repassed through a red-hot porcelain tube; nor is it decomposed at high temperatures by phosphorus, sulphur, nor even, according to the experiments of Saussure, by hydrogen (*Journal de Physique*, lv.), though it is stated, upon other authorities, that at high temperatures hydrogen does decompose it. When one volume of carbonic oxide is detonated with one of nitrous oxide, there result one volume of carbonic acid and one of nitrogen. (HENRY, *Ann. of Phil.*, N. S., viii. 299.) On this principle is founded a method of ascertaining the purity of nitrous oxide, it being implied, that that gas is free from nitric oxide. Let a given volume, say 100 measures, be exploded with slight excess of carbonic oxide,—if the nitrous oxide be pure, 100 measures of carbonic acid should be produced, and whatever is short of that proportion may be ascribed to impurity. None of the metals exert any action upon this gas, except potassium and sodium, which, at a red heat, burn in it by abstracting its oxygen, and carbon is deposited. Dr. Henry found, that when a mixture of carbonic oxide with more than half its volume of oxygen is exposed over mercury in contact with spongy platinum, to a temperature between 300° and 310° , it begins to be converted into carbonic acid, and, at a heat a few degrees higher, is quickly acidified. At common temperatures these mixtures are very slowly acted on. When carbonic oxide is added in an equal volume to a mixture of hydrogen and oxygen gases in explosive proportions, it prevents spongy platinum from causing detonation; but the gases slowly act on each other, and form water and carbonic acid. The platinum occasions mixtures containing less carbonic oxide to explode. (*Phil. Trans.*, 1824, p. 271.)

The composition of carbonic oxide is determined by the result of its combustion with oxygen, with which it forms carbonic acid. In this case, when *two* volumes of carbonic oxide and *one* of oxygen are acted on by the electric spark, detonation ensues, and *two* volumes of carbonic acid are produced: hence it follows, that carbonic oxide contains half as much oxygen, and *the same* quantity of carbon, as carbonic acid; if, therefore, we assume, that it is constituted of one volume of gaseous carbon, and one volume of oxygen, (the specific gravity of the vapour of carbon being 0·84, and the specific gravity of oxygen being 1·11,) the specific gravity of carbonic oxide should be $\frac{0\cdot84+1\cdot11}{2}=0\cdot97$,

which agrees with the experimental result: or

	Grains.
50 cubic inches of the vapour of carbon	= 12·7
50 " oxygen . . .	= 17·3
100 " carbonic oxide . .	= 30·

Assuming carbonic oxide to be a *protoxide of carbon*, the number 6 may be assumed as the equivalent of carbon, and carbonic oxide will consist of

	Gay Lussac.
Carbon . . . 1 . . 6 . . 42·9 . . 43·	
Oxygen . . . 1 . . 8 . . 57·1 . . 57·	
I 14 100·0 100·	

Or, by volume, as follows:—

Carbon.	Oxygen.	=	Carbonic Oxide.	or	Carbon. 6	=	Carbonic Oxide. 14
					Oxygen. 8		

It has been above observed (p. 163), that in order to assimilate the equivalent of carbon to that deduced from its specific heat, it would require that it should be assumed as 6×2 , or 12; in that case carbonic oxide would be (*car* + 2 *o*) and carbonic acid (*car* + 4 *o*), and the majority of the carbonates would become dibasic salts. In assuming the theoretical combining volume of carbon vapour to be half that of hydrogen, and to correspond with that of oxygen, I have been guided by Mitscherlich, as explained in a note referring to the constitution of carbonic acid. I have adopted the number 6 as the equivalent of carbon, consistently with the theoretical view of Dr. Prout. Dr. Turner employs the equivalent 6·13, and Mr. Graham 6·12. Dumas has lately shown that 6 is nearer the truth.

Carbonic oxide is sometimes represented as performing the part of an elementary base; uniting, for instance, with oxygen to form carbonic and oxalic acids: with chlorine to form chlorocarbonic acid, and with amide to form oxamide; hence, in regard to *oxalic acid*, the term *oxalyde* proposed for it by Berzelius.

CARBONIC OXIDE AND CHLORINE. OXYCHLORIDE OF CARBON. CHLOROCARBONIC OR CHLOROXICARBONIC ACID. PHOSGENE GAS. (*car* + *o* + *c*.)

—This gas was obtained by Dr. J. Davy (*Phil. Trans.*, 1812, p. 144), by exposure to solar light of a mixture of equal volumes of chlorine and carbonic oxide, hence its name, from *φως*, *light*, and *γεννέω*, to *produce*. It is also formed by exposing the mixed gases to ordinary daylight, but several hours are required for the purpose. When perfectly excluded from light these gases exert no mutual affinity. In the sunshine the mixture diminishes in bulk to half its original volume, and forms a compound of a very peculiar and pungent odour, but not disagreeable when considerably diluted. It reddens litmus; is soluble in water, and resolved by it into *carbonic and hydrochloric acid gases*. Alcohol takes up 12 times its volume, and acquires a peculiar taste, and the odour of the gas. The specific gravity of chlorocarbonic acid to hydrogen is as 50 to 1, and to common air as 3·472 to 1. 100 cubical inches weigh about 106 grains: at 32°, 100 cubical inches weigh 113·85 grains. (THOMSON.)

When tin or zinc are heated in one volume of this gas, they abstract and combine with the chlorine, and evolve one volume of carbonic oxide, hence chlorocarbonic acid consists of

Or, by volume

Carbon	1	6	12
Oxygen	1	8	16
Chlorine	1	36	72
<hr/>						
Chlorocarbonic acid		1		50		100

Carbon.	Chlorine.	=	Chloro-carbonic Acid.
Oxygen.			

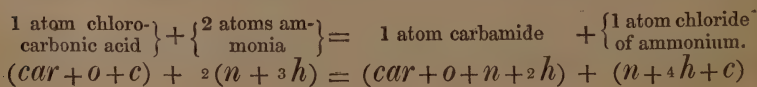
Chlorocarbonic acid therefore, in reference to the theory of substitutions, has been regarded as carbonic acid in which one equivalent of oxygen is replaced by one of chlorine.

CHLOROCARBONATE OF AMMONIA.—Chlorocarbonic acid condenses four volumes or two atoms of ammonia, producing a peculiar deliquescent compound of a white colour, which is resolved by the action of water into hydrochlorate and carbonate of ammonia. This salt is also decomposed by sulphuric, nitric, and hydrochloric acid, which evolve from it two volumes of hydrochloric and one volume of carbonic acid; it dissolves without effervescence in acetic acid, and sublimes unaltered, when heated in carbonic or sulphurous acid gas.

Its components are

Carbon	. 1 . . 6 . . 7·2	Chlorocarbonic acid	1 . . 50 . . 59·5
Oxygen	. 1 . . 8 . . 9·5		
Chlorine	. 1 . . 36 . . 42·8		
Hydrogen.	. 6 . . 6 . . 7·2	Ammonia	. . . 2 . . 34 . . 40·5
Nitrogen.	. 2 . . 28 . . 33·3		
	<hr/>		
	I 84 100·0	1	84 100·0

According to Regnault this compound contains sal-ammoniac and a compound of carbonic oxide and amide ($n+2h$): for 1 atom of chlorocarbonic acid and 2 atoms of ammonia contain the elements of carbamide and hydrochlorate of ammonia (or chloride of ammonium), as follows:—



CARBAMIDE, therefore, is a compound of

Carbon	. 1 . . 6 . . 20.0	} = 1 carbonic oxide	14 . . 46.8
Oxygen	. 1 . . 8 . . 26.8		
Nitrogen	. 1 . . 14 . . 46.6	} = 1 amide . . .	16 . . 53.2
Hydrogen	. 2 . . 2 . . 6.6		
<hr/> Carbamide	<hr/> 1 . . 30 . . 100.0		<hr/> 30 . . 100.0

CARBONIC ACID. FIXED AIR, AERIAL ACID. (*car* + 2 *o*) or *car'*,

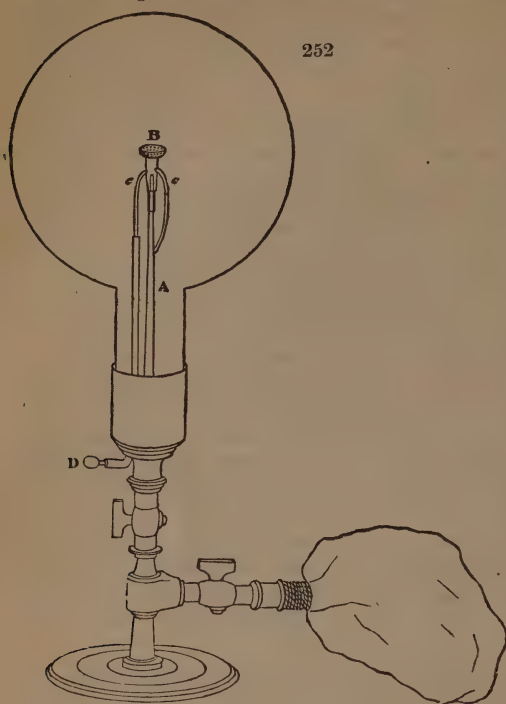
or CO₂ or C̄.—This important compound was discovered by Dr. Black, in 1757, and described by him under the name of *fixed air*, in his inaugural dissertation on magnesia. It may be obtained by burning carbon, either pure charcoal or the diamond, in oxygen gas; the oxygen suffers no change of bulk, so that the composition of carbonic acid may be learned by comparing its weight with that of an equal volume of pure oxygen.

Combustion of the Diamond.—The combustibility of the diamond seems first to have occurred to Newton. In the year 1694, the Florentine Academicians verified his anticipations, and proved its destructibility by heat by means of a burning lens. The *products* of its combustion were first examined by Lavoisier in 1772, and subsequently with more precision by Guyton Morveau, in 1785. (*Ann. de Chim.*, xxxi.) In 1797, (*Phil. Trans.*,) Mr. Tennant demonstrated the important fact, that when equal weights of diamond and pure charcoal were submitted to the action of red-hot nitre, the results were in both cases the same: and, in 1807, (*Phil. Trans.*,) the combustion of the diamond in pure oxygen was found by Messrs. Allen and Pepys to be attended with precisely the same results as the combustion of pure charcoal.

When the diamond is heated in the flame of the blow-pipe it soon begins to burn, and the combustion continues as long as the temperature is sufficiently high, but it does not produce heat enough, during its combination with the oxygen of the atmosphere, to maintain its combustion. If, whilst thus burning, it be introduced into a jar of pure oxygen, the combustion continues longer, and sometimes till the whole is consumed: the best support for it, in this experiment, is a small loop of platinum wire, or a very small and thin platinum spoon, perforated with many holes; in this it may first be intensely heated by the oxygen blow-pipe, and whilst burning, carefully immersed into a bottle of pure oxygen gas containing a little lime-water: a good cork, through which the wire of the spoon passes, should secure the mouth of the bottle: it will thus go on burning brilliantly for some time, and the formation of carbonic acid be shown by the milkiness of the lime-water.

The combustion of the diamond may be more perfectly effected by placing it upon a platinum capsule in a jar of pure oxygen inverted over mercury, and throwing upon it the focus of a burning lens. Sir H. Davy, when at Florence, in 1814 (*Phil. Trans.*, 1814, p. 558), used for this purpose the lens employed in the first trials on the action of solar heat on the diamond, instituted by Cosmo III., Grand Duke of Tuscany: he found that the diamond continued to burn in the oxygen, after being withdrawn from the focus, with so brilliant a light as to be visible in the brightest sunshine, and with very intense heat.

The following is another form of apparatus which may be employed for exhibiting the results of the combustion of the diamond. It consists



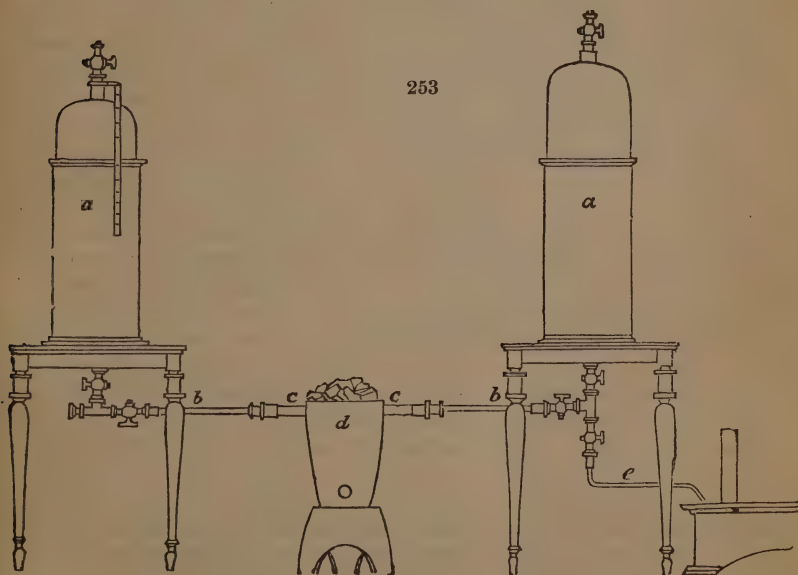
of a glass globe, of the capacity of about 140 cubical inches, furnished with a cap, having a large aperture; the stop-cock, which screws into this cap, has a jet A, rising from it, nearly into the centre of the globe; this is destined to convey a small stream of hydrogen, or other inflammable gas. Two wires, c c, terminate at a very little distance from each other, just above this jet, and are intended to inflame the stream of hydrogen by electrical sparks; one of them commences from the side of the jet, the other is enclosed and insulated nearly in its whole length in a glass tube: the tube and wire pass through the upper

part of the stop-cock, and the wire terminates on the outside in a ball or ring D, at which sparks are to be taken from the machine, either directly or by a chain. On the end of the jet is fixed, by a little socket, a small capsule B, made of thick platinum-foil. This capsule is pierced full of small holes, and serves as a grate to hold the diamonds. Its distance is about three quarters of an inch from the end of the jet; and the arm, by which it is supported, is bent round, so that the stream of hydrogen shall not play against it. The stop-cock screws by its lower termination on to a small pillar, fixed on a stand, and at the side of this pillar is an aperture, by which a bladder filled with gas may be connected with the apparatus.

On using the apparatus, the diamond is to be placed in the capsule; and then the globe being screwed on to the stop-cock, the latter is to be removed from the pillar and placed on the air pump; the globe is then to be exhausted, and afterwards filled with pure oxygen; or, lest the stream of oxygen in entering should blow away the diamond, the globe may be filled with the gas first, and then, dexterously taking out the stop-cock for a short time, the diamonds may be introduced, and the stop-cock replaced. The apparatus is then to be fixed on the pillar, and a bladder of hydrogen gas attached to the aperture. Now, passing a current of sparks between the wires, a small stream of hydrogen is to be thrown

in, which inflaming, immediately heats the diamonds and capsule white-hot; the diamonds will then enter into combustion, and the hydrogen may be immediately turned off and the bladder detached. The diamonds will continue to burn, producing a strong white heat, until so far reduced in size as to be cooled too low by the platinum with which they lie in contact. When the flame of hydrogen is used to heat the diamonds, it is evident a little water will be formed in the globe, but this is of no consequence except in attempts to detect hydrogen in the diamond; the inconvenience may be obviated, if required, by using the flame of carbonic oxide. As, however, no hydrogen has at any time been detected in the diamond, it is better to use that gas as the heating agent: for then the carbonic acid, produced by the combustion, is unmixed with that from any other source, and may be collected, and its quantity ascertained.

The following method of illustrating the products of the combustion of the diamond was employed by Messrs. Allen and Pepys (*Phil. Trans.*, 1807): *a a* are mercurial gasometers, one of which is filled with pure oxygen gas. The brass tubes *b b*, properly supplied with stop-cocks, issue

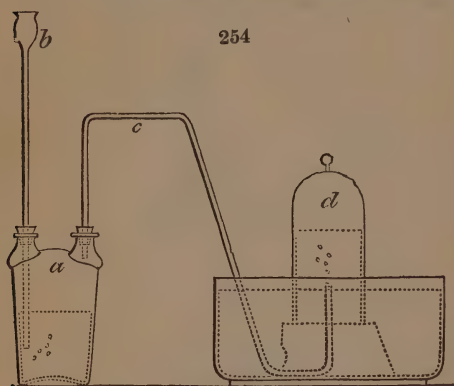


from the gasometers, and are connected with the platinum tube *c c*, which passes through the small furnace *d*. *e* is a glass tube passing into the mercurio-pneumatic apparatus, by which the gas may be drawn out of the gasometers into convenient receivers. A given weight of diamond is introduced into the centre of the platinum tube, which is then heated to bright redness, and the gas passed over it, backwards and forwards, by alternately compressing the gasometers. Carbonic acid is soon formed, and it is found that the increase of weight sustained by the oxygen is equivalent to that lost by the diamond; that the oxygen undergoes no

change of bulk; and that the results are, in all respects, similar to those obtained by a similar combustion of perfectly pure charcoal.

When *charcoal* is burned in oxygen, the phenomena of the combustion very much depend upon the nature of the charcoal, which, if well burned, and of a dense wood, glows with intense heat and gradually disappears, but if of a lighter wood, and especially if covered with portions of the bark, throws off jets of brilliant sparks, and furnishes one of the most striking experiments. A small piece of the purest graphite, such as is used for pencils, may also be burned in oxygen, and its combustion much resembles that of the diamond; it should first be carefully annealed by slowly heating it to redness in the flame of a spirit lamp, then attached to a loop of fine platinum wire, heated to whiteness in the oxygen blow-pipe, and in that state introduced into the oxygen, as above directed in regard to the diamond.

Preparation, Liquifaction, and Solidification of Carbonic Acid Gas.—For all the common purposes of experiment, carbonic acid is best procured



by the action of dilute hydrochloric acid upon white marble, which, in small fragments, is introduced into the two-necked bottle *a*, and covered with water; hydrochloric acid is then slowly poured down the funnel *b*, which causes an immediate effervescence, and the gas passes through the bent tube *c*, into the inverted jar *d*. When the action ceases, it may be renewed by the addition of fresh acid, until the whole

of the marble is dissolved. When large quantities of carbonic acid are required, chalk and dilute sulphuric acid are generally resorted to, and for some particular purposes bicarbonate of soda and dilute sulphuric acid are used.

Carbonic acid may be collected over water, but must be preserved in vessels with glass stoppers, since water, at common temperature and pressure, slowly absorbs it. When required perfectly pure, the gas should be first washed by passing it through water, and then deprived of hygro-metric moisture by passing it through a long tube filled with fragments of fused chloride of calcium. Carbonic acid is a colourless gas, of a slightly sour odour, considerably heavier than atmospheric air, its specific gravity being about 1.52. Compared with hydrogen its specific gravity is as 22 to 1, and 100 cubic inches weigh 47.26 grains, (49.9780 grains at the temperature of 32°. THOMSON.)

Liquid Carbonic Acid.—At all common temperatures and pressures carbonic acid retains the gaseous state, but when duly subjected to great pressure it becomes liquid. To effect its liquifaction Mr. Faraday proceeded as follows:—A strong tube, of about one-fourth of an inch diame-

ter and eight inches long, being bent, at about two inches from its end, to an obtuse angle, and sealed at the shorter end, sulphuric acid was poured in through a small funnel, so as not to soil the larger leg, which was then loosely filled with fragments of carbonate of ammonia, and also hermetically sealed; the acid was then made to run upon the salt, and the evolved carbonic acid gradually appeared in the liquid form. The utmost precautions are here necessary to guard against explosion: such as goggles and a glass mask to preserve the face and eyes, and thick gloves for the hands: the tubes should also never be touched without great care; for sometimes, after having held the fluid safely for weeks together, they have exploded from some very slight increase of temperature. (*Phil. Trans.*, 1823.)

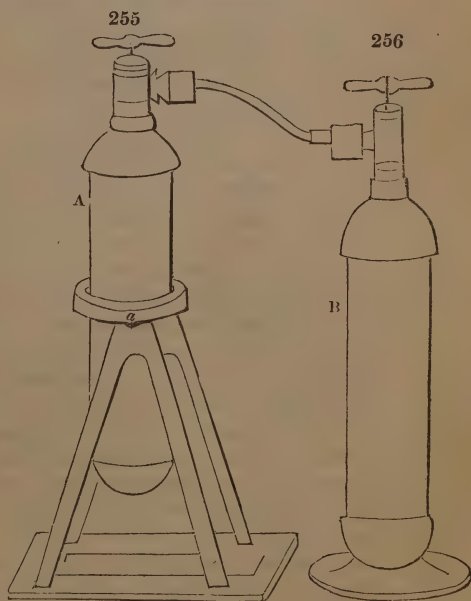
The liquifaction of carbonic acid is now conducted upon a large scale, especially by Mr. Addams, of Kensington, who sometimes has treasured up, in suitable reservoirs, as much as nine gallons at one time, and has even made it an article of commerce. He has been kind enough to give me the following details upon this subject:—

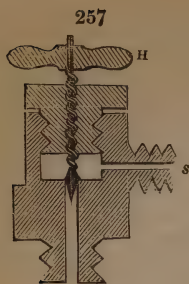
The apparatus he employs is of two kinds: the first, or simple mode, is dependent upon the chemical forces disengaging the carbonic acid, from the materials used under confinement, as originally suggested by Faraday; and in this, the general construction of the instruments employed is similar to those of M. Thilorier, although in respect to form, material, and structure, of the valves, there is considerable difference, being more simple in arrangement, and lighter in proportion to strength.

The second, or improved method, is partly dependent upon the chemical forces, and partly effected by mechanical compression with powerful pumps.

For either process two strong wrought-iron vessels are required, one is named the *generator*, A (fig. 255), the other the *receiver* B (fig. 256); each of these vessels is a cylinder two feet long and four inches internal diameter, having hemispherical ends, and of such strength as to bear proving to more than 4000 lbs. upon a square inch.

The generator is furnished with an axis *a*, and mounted upon a cast iron frame so as to revolve in a vertical plane *a a* (fig. 260). At one end of each vessel is screwed on a peculiar valve (fig. 257), so constructed as





to prevent leakage in the screw part, when the valve is opened. The lower, or valve part, of the central screw, to which the handle *H* is applied, is formed into a cone, which when screwed down shuts up the passage into the vessel; but when the screw is raised or turned backwards, there is a passage from the vessel and out of the side vent *s*; at the same time the upper conical shoulder of the valve comes into its seat in the plug-piece through which the valve-screw itself passes, and thus prevents escape of gas by the sides of the screw.

The *generator* is simply a hollow vessel within, but the *receiver* has a slender pipe, open at both ends, inserted into the valve-plug, and descending nearly to the bottom, as shown by *T T* (fig. 258) in the section.



The materials used in the production of liquid carbonic acid are as follows, namely, water at 100° , bicarbonate of soda in fine powder, and sulphuric acid of full commercial strength; and for a generator of the dimensions before described the proportions are, water 6.25 lbs., bicarbonate 2.75 lbs., and sulphuric acid 1.47 lbs. These proportions leave an excess of alkaline salt, which is desirable in order to prevent the action of the acid upon the metal of the generator.

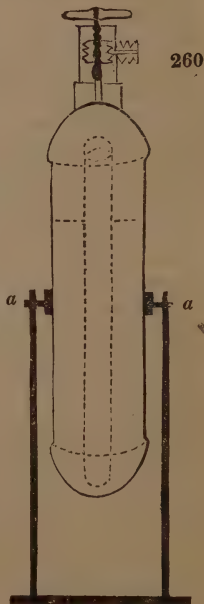
To charge the generator, the valve plug is taken out, and a funnel inserted in its place; through this a part of the tepid water is introduced, then the carbonate, and afterwards the remainder of the water, and then stirred with a rod.

The acid is next put in, but to prevent its action before the valve plug is replaced, it is contained in a brass tube (fig. 259), of such diameter and length as to hold the measure of acid and also

259



pass through the orifice in the neck of the generator, and to stand erect with its open end above the saline mixture within, as shown in fig. 260. The valve-plug is now firmly screwed to the generator, and the whole inverted and turned over and over, by which the acid comes into contact with the carbonate of soda, and the mixture is completely effected. Then by allowing the generator to stand a few minutes erect, with the valve end upwards, the liquified carbonic acid, being lighter than the resulting sulphate of soda, rises, and floats as a distinct stratum. A connection is then made between the gene-

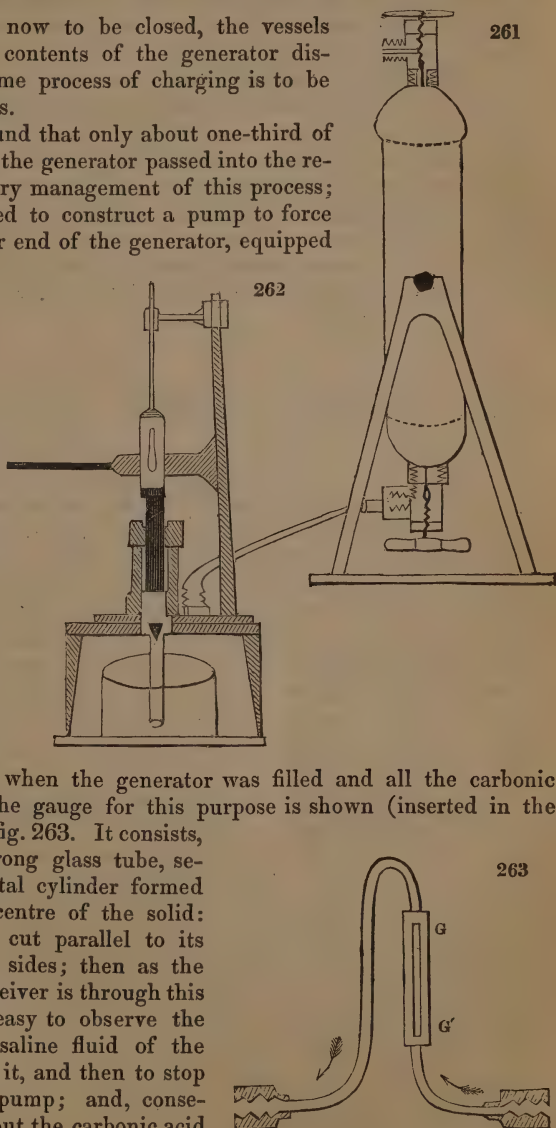


rator and receiver by an union pipe, as at figs. 255 and 256, and then the valves of both vessels being opened, the carbonic acid passes, by a process of rapid distillation, from the former into the latter. This transfer is accelerated in proportion as the temperature of the two vessels differs; hence warm water is employed in charging; an increase of heat also ensues by the acid mixing with the water; the receiver also should be put into cold or iced water.

The valves are now to be closed, the vessels separated, and the contents of the generator discharged, and the same process of charging is to be repeated many times.

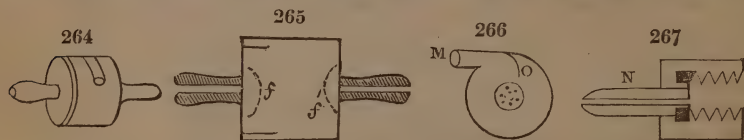
Mr. Addams found that only about one-third of the carbonic acid of the generator passed into the receiver in the ordinary management of this process; he was, therefore, led to construct a pump to force water into the lower end of the generator, equipped with two valves, as figs. 261 and 262; and thus by filling the generator, the whole of the liquid carbonic acid is transferred into the receiver, and that too without the cooling of the receiver with ice; and by this plan an economy equal to two-thirds in material and time is effected. But in order to use

a pump to use a gauge to observe when the generator was filled and all the carbonic acid displaced. The gauge for this purpose is shown (inserted in the union-pipe) at G G', fig. 263. It consists, essentially, of a strong glass tube, secured within a metal cylinder formed by boring out the centre of the solid: this last has slits cut parallel to its length on opposite sides; then as the passage into the receiver is through this glass gauge, it is easy to observe the instant when the saline fluid of the generator rises into it, and then to stop the action of the pump; and, consequently, no liquid but the carbonic acid enters the receiver.



He has attached a gauge of similar construction to a double-valved receiver, and with it is enabled to see the carbonic acid at any time, to measure the quantity transferred from this vessel into others, and to obtain certain useful information respecting the quantity produced by different modes of management.

Within the receiver, when charged, there is liquid carbonic acid below, and highly condensed gas above it: upon opening the valve the expansion of the gas forces the liquid up the central tube *TT* (fig. 258), and then a part of it instantly passes into the state of gas at the orifice of the outlet *s* (fig. 257), and another portion is frozen into a white snow-like solid, affording a beautiful instance of the sudden transference of heat when a liquid expands into a gas. This white matter, or solid carbonic acid, is blown out in finely-divided particles, and to collect it, an ingeniously constructed recipient or *draw-out box* is used, being the contrivance of M. Thilorier. It consists of a brass cylindrical case (fig. 264), having tubular handles affixed to its ends. Plates of pierced brass are fixed before the outlet of each handle, as shown by *f'f* (fig. 265); these act as sieves to keep back the solid acid and allow the gas to pass out.



The box has a short tube joined to the side, as in section fig. 266, *M*, so as to form a tangent to the inner circle of the case. And opposite to this pipe is placed a bent plate of brass, *O* (fig. 266), in order to prevent the violence of the intruding gas from blowing the solid matter into such fine powder as would enable it to pass through the perforated discs. For the purpose of taking out the solid, the box is made separable by one end sliding a little within the other, and retainable together by two obliquely grooved holders placed on opposite sides of the joint. This draw-out box is united to the receiver by the union-piece (fig. 267), the nozzle *N*, having a small hole through it, and upon this the tangent-tube of the box fits.

From 2·75 lbs. of bicarbonate of soda of average quality, Mr. Addams obtains about 19000 cubic inches of carbonic acid of ordinary pressure and temperature: by the first method, without the pump, 13000 of these are left in the generator, and, of course, escape on opening, unless the receiver be kept colder and a longer time allowed for the transfer than is convenient in a general way of management. He finds that about 12·5 cubic inches of liquid carbonic acid are conveyed into the receiver from each charge of the generator, provided the temperature of the receiver be at 54°. But when the pump is employed the only loss of acid is that which is entangled with the sulphate of soda, and which generally measures 1100 cubic inches, under atmospheric pressure; and in this way about 37 cubic inches of liquid carbonic acid are sent into the receiver, at each charging, instead of 12·5.

The tension of carbonic acid gas as it exists above the liquid depends

upon the temperature, and Mr. Addams has given the pressures through a considerable range of the thermometer, namely, from zero to 150° , at intervals of each 5° . The following table includes the force for each successive 10th degree; by which it will be seen, that, similar to vapours of all kinds resting upon their respective liquids, the tension increases in a higher ratio than the temperatures. He employed a pressure gauge of 43 inches in length, in the experiments which afforded data for this table; and many of the results were confirmed by a kind of loaded safety valve*.

Temperature.	Pressure in lbs. per sq. inch.	Pressure in Atmospheres per sq. inch.	Temperature.	Pressure in lbs. per sq. inch.	Pressure in Atmospheres per sq. inch.
Zero	270.9	18.06	80°	741.3	49.42
10°	300.	20.	90	837.6	55.84
20	346.65	23.11	100	934.8	62.32
30	398.1	26.54	110	1040.25	69.35
40	457.35	30.49	120	1151.7	76.78
50	520.05	34.67	130	1264.65	84.31
60	586.35	39.09	140	1379.55	91.97
70	658.05	43.87	150	1495.65	99.71

Liquid Carbonic Acid is limpid, colourless, and extremely fluid. Its specific gravity at 32° is 0.83: it distils readily and rapidly at the difference of temperature between 32° and 0° . Its refractive power is much less than that of water. No diminution of temperature alters its appearance. In Mr. Faraday's endeavours to open the tubes at one end, they always burst into fragments with powerful explosion. Mr. Brunel endeavoured to apply this liquid as a mechanical agent for the production of motive power: of this attempt a short account will be found in the *Quarterly Journal* (Old Series, xxi. 131).

Liquified carbonic acid exhibits a remarkable property in respect to its expansibility by heat, in which it appears, from M. Thilorier's statement (*Ann. de Chim. et Phys.*, LX. 427), to exceed even that of the gaseous acid, or of air. Thus from (0° to $+30^{\circ}$ centigrade) 32° to 86° (Fahrenheit), its bulk increases from 20 to 29, which is 4 times greater than the dilatibility of air within the same range. From 0° to $+30^{\circ}$ (cent.) the pressure of the vapour furnished by the liquified gas, rises, according to Thilorier, from 36 to 73 atmospheres, which is one atmosphere of increase for each centigrade degree. Liquid carbonic acid is insoluble in water and in the fat oils, but it is soluble in all proportions in alcohol, ether, oil of turpentine, and carburet of sulphur.

A jet of liquid carbonic acid, emitted upon the bulb of a spirit thermometer, sinks it to -90° (cent.), but the general frigorific effects do not correspond with this depression of temperature, in consequence of the almost entire want of conducting power in the gas, and its little capacity for heat. But as the case is different with regard to *vapours*, Thilorier tried the effect of a jet of liquid carbonic acid mixed with ether, and in this way he succeeded in producing a *cold blow-pipe*, which froze 50 grammes of mercury in a small glass capsule in a few seconds. Mr.

* In this table the atmospheric pressure is assumed to be = 15 lbs.

Addams informs me that at common temperatures liquid carbonic acid acts with extreme slowness upon potassium and sodium, requiring a month to convert a piece of potassium, of the size of a pea, into carbonate of potassa: he observes that the potassium apparently derives its requisite equivalent of oxygen from the conversion of carbonic acid into carbonic oxide, inasmuch as no carbon is deposited when proper precautions have been taken to deprive the acid of water by fused chloride of calcium.

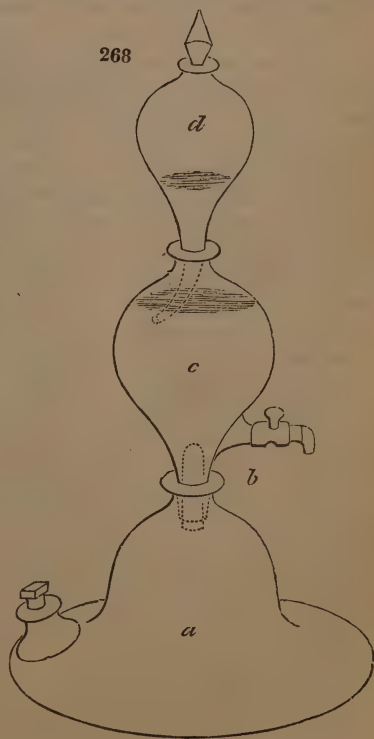
Solid Carbonic Acid.—Thilorier first showed that carbonic acid may be obtained in a *solid* form by suffering a jet of the liquid acid to issue into a small phial, which immediately was lined by a white flocculent powder, consisting of the carbonic acid solidified or frozen by the intense cold resulting from its own expansion. It is easily obtained in large quantity by the methods above described. In the solid state it moves about upon any polished surface, like a drop of water upon white-hot iron, and slowly disappears. Mr. Addams found the surfaces from which it had evaporated, in a negatively electrical state. When handled it feels like snow, and owing to its low conducting power it does not evaporate very rapidly nor feel extremely cold, though its actual temperature is probably as low as 148° below the 0° of Fahrenheit. When a little mercury is put into a saucer and covered by solid carbonic acid, the addition of a few drops of good ether forms a semifluid mass, by the contact of which the mercury is immediately frozen. In this way Mr. Addams succeeded in freezing ten pounds of mercury in less than eight minutes; and in further illustration of the extraordinary relations of this substance, he informs me that he has kept a large lump of the solid carbonic acid for a minute, in a red-hot crucible, and afterwards frozen a pound of mercury with it. When a piece of the solid acid is put into a gas bottle, it gradually becomes gas, which may be collected as usual over water; or its conversion into the gaseous state may be more strikingly observed by letting up a small piece of it into an inverted jar of water. The following modification of this experiment I first saw performed by Professor Graham. A tall stoppered air-jar is inverted in the pneumatic trough, and half filled with oxygen; a piece of solid carbonic acid is then let up into it, by which the lower half of the jar soon becomes filled with very cold carbonic acid gas; if the glowing wick of a taper, attached to a long wire, be then plunged through the upper opening of the jar into the oxygen, it is instantly kindled into flame, but extinguished by causing it to descend into the inferior atmosphere of carbonic acid; and by a little care the wick may be left glowing, and then lifted into the oxygen, when it again bursts into flame: this alternate extinction and reproduction of flame may in this way be many times repeated.

Properties of Carbonic Acid Gas.—This gas is perfectly unrespirable, for on attempting to breathe it in a pure state the epiglottis is spasmodically closed, and no air entering the lungs, suffocation is the direct consequence. When it is so far diluted with air as to admit of being received into the lungs, it then operates as a narcotic poison, producing drowsiness and insensibility, and this, even when a candle will burn in the mixture. (CHRISTISON.) Hence the danger of a confined room in which a pan of burning charcoal is placed. Butterflies, and other insects,

of which it is desired to preserve the colours unimpaired, may sometimes be conveniently suffocated by this gas. Carbonic acid immediately extinguishes the flame of a taper, and this even when considerably diluted with atmospheric air. In this way its weight may be conveniently shown by placing a lighted taper at the bottom of a tall glass jar, and then pouring the gas out of a bottle into it, in the manner of a liquid; it descends, and extinguishes the flame, and will remain for some time in the lower part of the vessel. Like other gases, however, notwithstanding its specific gravity, it soon blends with, and diffuses itself through, the mass of surrounding air. In wells, and in some caverns, carbonic acid frequently occupies the lower parts, while the upper parts are free from it. The miners call it *choak damp*. In these cases it issues from crevices in the earth, and is produced by unknown sources. In consequence also of its weight, it may be collected without the pneumatic apparatus, as it issues from a tube passed near the bottom of a dry bottle: it soon displaces the common air, and may be traced, flowing over the neck of the bottle, by holding a taper to it, which is then extinguished. (See this mode of collecting gas described at p. 366.)

When water is agitated in carbonic acid, it takes up its own volume of the gas at common temperature and pressure, and acquires a very slight increase of specific gravity. Under a pressure of two atmospheres it dissolves twice its volume, and so on. It thus becomes brisk and tart, and reddens delicate vegetable blues. If litmus paper, thus reddened, be exposed to the air, the blue colour returns as the acid evaporates; hence an easy distinction between the paper reddened by any of the more fixed acids in which the change of colour is permanent. In the same way, infusion of litmus thus reddened becomes blue when the carbonic acid is expelled by boiling. By freezing, boiling, or exposure to the vacuum of the air-pump, the gas is given off, and it gradually makes its escape when exposed to air, collecting in small bubbles upon the sides of the containing vessel, and passing off with especial rapidity when any foreign substances are thrown in, or when any substance is dissolved in the water; thus it is, that sugar added to soda-water, cyder, champagne, or other similar carbonated liquors, occasions in them an immediate and abundant effervescence.

Porter, ale, cyder, and many other beverages, derive their brisk-



ness from carbonic acid. The effervescent quality of many mineral waters is also referable to the presence of this gas, and they are often imitated by condensing carbonic acid into water, either by a condensing pump, of which a description is given by Mr. Pepys (*Quarterly Journal of Science and Arts*, iv. 305), or by a *Nooth's apparatus*, as represented in the preceding wood-cut (fig. 268). It consists of three vessels, the lowest, *a*, flat and broad, so as to form a steady support; it contains the materials for evolving the gas, such as pieces of marble and dilute hydrochloric acid, of which fresh supplies may occasionally be introduced through the stopped aperture. The gas passes through the tube *b*, in which is a glass valve opening upwards, into the vessel *c*, containing the water or solution intended to be saturated with the gas, and which may occasionally be drawn off by the glass stop-cock. Into this dips the tube of the uppermost vessel *d*, which occasions some pressure on the gas in *c*, and also produces a circulation and agitation of the water. At the top of *d* is a heavy conical stopper, which acts as an occasional valve, and keeps up a degree of pressure in the vessels.

The presence of carbonic acid is instantly detected by *lime water*, which it renders turbid, and causes a deposit of a white powder, which is *carbonate of lime*. The addition of water saturated with carbonic acid, to lime-water, also occasions a milkiness from the same cause. If excess, either of the gas or of its aqueous solution, be added to the lime-water, the precipitate is re-dissolved, carbonate of lime being soluble in carbonic acid. (See *Lime*.)

As all common combustibles, such as coal, wood, oil, wax, tallow, &c., contain carbon as one of their component parts, so the combustion of these bodies is always attended by the production of carbonic acid. It is also produced by the respiration of animals; hence it is detected, often in considerable proportion, in crowded and illuminated rooms, which are ill ventilated, and occasions difficulty of breathing, giddiness, and faintness. In the atmosphere it may also be detected, as has already been mentioned (page 448). Saussure found it in air from the summit of Mont Blanc; and Humboldt discovered it in air brought by Garnerin from a height of twenty thousand feet, to which he had ascended in a balloon. Its production in the lungs is easily shown, by blowing the expired air through lime-water by means of a small tube; it becomes milky, and soon deposits carbonate of lime. The quantity of carbonic acid ejected from the lungs at each ordinary expiration varies a little at different times of the day. (See *Respiration*.) According to Dr. Prout, it amounts on an average to 3.45 per cent. of the expired air, its limits being 3.3 and 4.1 per cent.

As carbonic acid is often retained in combination by feeble affinity, so it is evolved from some of the *carbonates* by the simple operation of heat. Thus chalk, when heated, gives out carbonic acid, and becomes *quicklime*, but in these cases its escape is generally facilitated by the copresence of air or aqueous vapour; in other cases the carbonates may be heated to redness without the slightest tendency to the evolution of carbonic acid, as is the case with the carbonates of potassa and soda. Carbonic acid is also displaced by most of the other acids; and if dilute nitric, hydrochloric, or sulphuric acid be poured upon the carbonates, the presence of carbonic acid is indicated by *effervescence*.

Carbonic acid retards the putrefaction of the greater number of animal substances: applied to the roots of vegetables in aqueous solution, it is generally propitious to their growth, as will be more fully shown in a future chapter. Most plants thrive in an atmosphere containing not more than a tenth or twelfth part of carbonic acid; and under certain circumstances, which will afterwards be explained, they decompose it, and evolve oxygen.

At high temperatures, carbonic acid is decomposed by several of the metals, and converted into carbonic oxide; and potassium and sodium, when sufficiently heated, burn in it, and are converted into potassa and soda, whilst the carbon or charcoal of the gas is thrown down in the solid form. There are some other substances which, at high temperatures, are capable of decomposing carbonic acid, and abstracting part of its oxygen; thus, if a mixture of two parts of hydrogen and one of carbonic acid, by volume, be passed through a red-hot tube in the apparatus represented at p. 431, water is formed, and carbonic oxide passes into the receiver *d*, mixed with the excess of hydrogen. Dr. Henry also found that by passing a succession of electric sparks through carbonic acid confined over mercury, a portion of it was resolved into carbonic oxide and oxygen. (*Phil. Trans.*, 1809, 448.) When the carbonic acid which escapes decomposition has been washed out by solution of potassa, an electric spark inflames the residuary mixture, the oxygen and carbonic oxide again uniting and reproducing carbonic acid.

Phosphorus, when heated in carbonic acid, does not decompose it; whence it might be inferred that carbon possessed a stronger affinity for oxygen than phosphorus; and such an inference is sanctioned by the decomposition of phosphoric acid, at high temperatures, by charcoal: but if complex attraction be brought into action, the case is altered, as was first shown by Tennant (*Phil. Trans.*, 1791, p. 182), and afterwards by Pearson (*Phil. Trans.*, 1792, p. 280). Thus it is, that certain carbonates are decomposed, at high temperatures, by phosphorus: if the vapour of phosphorus be passed over ignited carbonate of lime, or carbonate of soda, charcoal is deposited, and phosphate of lime or phosphate of soda produced.

If carbonic acid be passed over red-hot charcoal, it becomes converted into carbonic oxide, by taking up an additional proportion of base. The blue flame, often seen upon the surface of a charcoal fire, arises from the combustion of the carbonic oxide formed in this way; the air entering at bottom, forms carbonic acid, which, passing through the red-hot charcoal, becomes converted into carbonic oxide. At a bright red heat, iron and zinc decompose carbonic acid, by abstracting a portion of its oxygen, and forming oxide of iron or of zinc, and carbonic oxide.

It has been above stated, that when carbon is burned in oxygen gas, carbonic acid is formed equal in volume to that of the oxygen, so that the difference of specific gravity between oxygen and carbonic acid leads to the quantity of carbon which it contains, and the weight of pure carbon taken up by a given bulk of pure oxygen gas, may thus be directly determined by experiment. Assuming the specific gravity of carbon vapour to be 0.84, and that of oxygen gas 1.11, and that a volume of carbonic

acid consists of one volume of oxygen, and half a volume of carbon vapour, its specific gravity should be $(1.11 + .42) = 1.52$; or

		Grains.
50	cubic inches of carbon vapour, weighing	12.7
100	„ oxygen gas „	34.6
100	„ carbonic acid should weigh	47.3

Both these statements closely agree with the experimental result; carbonic acid, therefore, consists of

						Allen and Pepys.
Carbon	1	6	27.27	28.6		
Oxygen	2	16	72.73	71.4		
Carbonic acid	1	22	100.00	100.0		

Or it may be represented by volume thus* :—

Carbon. 6	Oxygen. 8	=	Carbonic Acid.
	Oxygen. 8		22

CARBONIC ACID AND AMMONIA. CARBONATE OF AMMONIA. ($A + car'$).
—When one volume of carbonic acid and two volumes of ammonia are mixed in a glass vessel over mercury, the gases are slowly condensed into a white crystallized solid, which lines the interior of the vessel, and which has been termed *carbonate of ammonia*. The product must at all events

* It has been customary to represent carbonic acid as a compound of *one* volume of the vapour of carbon and *one* volume of oxygen, the *two* volumes being condensed into *one* of carbonic acid, and, upon this principle the specific gravity of the vapour of carbon, in reference to the specific gravity of hydrogen, has been assumed as 6 to 1, or in reference to that of oxygen as 6 to 16. Upon this hypothesis, therefore, a volume of *carbonic oxide* would consist of one volume of the vapour of carbon and half a volume of oxygen, or

Carbon. 6	Oxygen 8	=	Carbonic Oxide.
			14

and a volume of *carbonic acid* would consist of one volume of carbon vapour and one volume of oxygen, or

Carbon. 6	Oxygen. 16	=	Carbonic Acid.
			22

But, as observed by Mitscherlich (*Lehrbuch der Chemie*, i. 84), this view of the specific gravity of carbon vapour is incon-

sistent with analogous gaseous combinations, and, as we cannot determine the point *experimentally* (as with sulphur and phosphorus), analogy is our only guide. And as we find, in all other cases, that when *one* volume of one gas combines with *one* volume of another, no condensation ensues (one volume of nitrogen and one of oxygen forming *two* of nitric oxide, and one volume of hydrogen and one of chlorine forming *two* volumes of hydrochloric acid, &c.) but that, on the other hand, condensation does ensue when one volume of one gas combines with *half* a volume of another (one volume of nitrogen and half a volume of oxygen forming *one* volume of nitrous oxide, and one volume of hydrogen and half a volume of oxygen forming one volume of steam), so it is probable that one volume of carbonic oxide is constituted of half a volume of carbon vapour and half a volume of oxygen; and that one volume of carbonic acid is constituted of half a volume of carbon vapour and one volume of oxygen. Upon this view of the subject, therefore, the specific gravity of carbon vapour would be 0.84 instead of 0.42; or, in reference to hydrogen, 12 instead of 6; and, as far as the theory of *volumes* is concerned, carbon would thus resemble oxygen.

contain the elements of ammonia and carbonic acid in the following proportions:—

Ammonia	. . . 1	. . . 17	. . . 43.5
Carbonic acid	. . . 1	. . . 22	. . . 56.5
	<hr/> 1	<hr/> 39	<hr/> 100.0

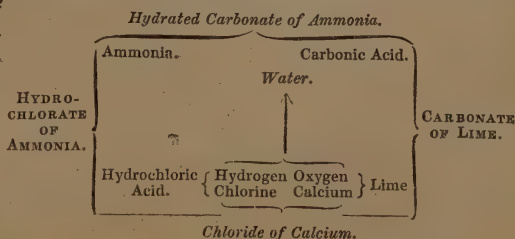
The above results, however, are only obtained when the gases are perfectly dry, for if any moisture be present more carbonic acid is taken up, and a sesqui or bicarbonate of ammonia result. This apparently anhydrous salt has not been accurately examined, but as there is no other instance of the direct union of ammonia with an anhydrous oxyacid, it has been suggested by Dumas that it may be an amide, or a compound of amidogen, carbonic oxide, and water: for it is obvious that the ultimate elements of the supposed neutral carbonate of ammonia (namely $n+3h+car+2o$) may be arranged as $(n+2h)+(car+o)+(h+o)$.

BICARBONATE OF AMMONIA. ($A+2car'$).—If water be present, ammonia and carbonic acid condense each other in equal volumes, and consequently a bicarbonate is the result; but it does not exist in an anhydrous state. It is also formed when the common carbonate is kept for some time exposed to air in imperfectly closed vessels, in which case it loses ammonia, and becomes nearly inodorous, and less soluble in cold water. When carbonic acid is passed through a saturated aqueous solution of the common carbonate, this salt is also produced, and may be brought to crystallize; it forms right rhombic prisms, soluble in about 8 parts of cold water; inodorous, and of little taste; containing, according to Berzelius, 22.7 per cent. of water. The salt consists, therefore, of

Ammonia 1	. . . 17	. . . 21.5	. . . R. Phillips.	21.16
Carbonic acid 2	. . . 44	. . . 55.7	. . .	55.50
Water 2	. . . 18	. . . 22.8	. . .	23.34
Bicarbonate of ammonia	1	<hr/> 79	<hr/> 100.0		<hr/> 100.00

In reference to the ammonium theory this salt has been termed a bicarbonate of oxide of ammonium, in which case the elements of one of the atoms of water must be supposed to have combined with those of the ammonia to form oxide of ammonium; and under this view the following would be the constitution of the salt $(n+4h+o)+2(car+2o)+(h+o)$. Graham calls it a carbonate of water and of oxide of ammonium, and represents it as follows. $(car+2o)+(h+o)+(n+4h+o)+(car+2o)$

SESQUICARBONATE OF AMMONIA. ($A+1\frac{1}{2}car'$).—The carbonate of ammonia of commerce is generally met with in cakes broken out of the subliming vessel, being obtained by sublimation from a mixture of sulphate or hydrochlorate of ammonia, and carbonate



of lime. When the hydrochlorate is used, the results of the decomposition are carbonate of ammonia, water, and chloride of calcium, the two former being in combination, so that a *hydrated carbonate of ammonia* is always obtained. Supposing the materials perfectly dry, the water is formed by the union of the hydrogen of the hydrochloric acid with the oxygen of the lime, as shown in the preceding diagram.

Phillips has shown (*Quarterly Journal*, vii. 294), that this carbonate of ammonia consists of

Ammonia	1	. . .	17	. . .	28.8
Carbonic acid . . .	1½	. . .	33	. . .	56.0
Water	1	. . .	9	. . .	15.2
<hr/>					
Sesquicarbonate of ammonia	1		59		100.0

As far, therefore, as relates to the proportion of the carbonic acid to the ammonia, this salt is intermediate between the carbonate and bicarbonate, or a *sesquicarbonate of ammonia*. Its odour is pungent; its taste hot and saline; it reddens turmeric, and has an alkaline reaction upon other vegetable colours. It is much used as a stimulant and antacid in medicine, and is commonly called *smelling salts*. A pint of water at 60° dissolves rather less than four ounces. This solution is directed in the *Pharmacopœia*, under the name of *Liquor Ammonia Sesquicarbonatis*. If a hot saturated solution of this salt be made in a close vessel, and suffered to cool, it deposits octoëdral crystals. Exposed to air, it loses ammonia, and becomes the hydrated bicarbonate above described.

CARBON AND CHLORINE. CHLORIDES OF CARBON.—For our knowledge of the compounds of carbon with chlorine we are indebted to Mr. Faraday (*Phil. Trans.*, 1821, p. 47). The circumstances under which they combine have been more recently investigated by Regnault (*Ann. de Ch. et Ph.*, LIX. 151, and LXX. 104). By exposing carburetted hydrogen, mixed with great excess of chlorine, to the action of light, a white crystalline substance is formed, which, when purified by washing with water, is a *perchloride of carbon*. It is formed as follows:—A glass vessel, capable of holding about 200 cubic inches, is properly mounted, with a stop-cock, and exhausted upon the air-pump: it is then nearly filled with chlorine, and afterwards placed in connexion with a jar of olefiant gas standing over water, and, as much as can enter having passed in, the cocks are shut, and the whole left for a short time: when the fluid compound of chlorine and carburetted hydrogen (described further on) has formed, the cocks are reopened, and a fresh portion of carburetted hydrogen rushes in, in consequence of the condensation which has taken place; this is left, as before, to combine with the remaining chlorine, and the process continued, until no further action ensues, and the vessel is, in fact, full of carburetted hydrogen: chlorine is then similarly admitted, in repeated portions, and, ultimately, a quantity of the liquid hydrochloride of carbon is obtained, with an atmosphere of chlorine above it: in this state it is exposed to the direct rays of the sun. The chlorine speedily disappears, and hydrochloric acid is formed: this is absorbed by the admission of a little water; another atmosphere of chlorine is then admitted, and exposure to the sun repeated; by continuing these opera-

tions, the whole of the hydrogen is at length abstracted in the form of hydrochloric acid, and crystals are formed in the liquid; these are to be collected, washed, and pressed between bibulous papers, then introduced into a glass tube, and sublimed by a spirit-lamp; the pure substance, with water, will rise at first, but the last portions will be partially decomposed, hydrochloric acid will be liberated, and charcoal left. The sublimed portion is then to be dissolved in alcohol, and poured into a weak solution of potassa, by which the substance is thrown down, and the hydrochloric acid neutralized and separated; then wash the substance with repeated affusions of water, collect and dry it, first between folds of paper, and then in the exhausted receiver of the air-pump. If quite pure, it sublimes without any change, and a small portion dissolved in ether gives no precipitate with nitrate of silver.

SESQUICHLORIDE OF CARBON ($car + 1\frac{1}{2}c$) thus purified is nearly tasteless; its odour resembles camphor; its specific gravity is about 2; it is a non-conductor of electricity, and powerfully refracts light. It is volatile, and in close vessels fuses at 320° ; it boils at 360° , and may be distilled without decomposition: its vapour again condenses in crystals as it cools. It is not very combustible, but burns when held in the flame of a spirit-lamp, with the emission of much smoke and acid fumes. It burns vividly in oxygen gas. It is insoluble in water, but readily soluble in alcohol and ether; these solutions deposit arborescent and quadrangular crystals. It also dissolves in volatile and fixed oils. It is scarcely acted upon by alkaline and acid solutions, but most of the metals decompose this substance at a red heat. Potassium burns brilliantly in its vapour, causing the deposition of carbon, and the production of chloride of potassium. The metallic oxides also decompose it at high temperatures, producing metallic chlorides, and carbonic acid or oxide, according to the proportion of oxygen present; no water is produced, showing the absence of hydrogen in the compound. It appears, from various analytical experiments upon this compound, among which may be mentioned its decomposition by passing it through red-hot peroxide of copper, that it is a *sesquichloride of carbon*, consisting, therefore, of

Carbon	1	. .	6	. .	10
Chlorine	$1\frac{1}{2}$. .	54	. .	90
Sesquichloride of carbon	1		60		100

This compound is represented by Regnault by the formula ($2\ car + 3\ c$), the density of its vapour as determined by experiment being 8.157, or 120 in reference to hydrogen as=1, and as

		Sp. Gr.
1 volume carbon	} = 2 atoms	0.84
vapour		
3 volumes chlorine	= 3 atoms (2.47×3)	7.41
1 volume vapour	} = 1 atom	8.25
of sesquichloride		
of carbon		

Carbon.	Chlorine.	Sesqui- chloride of Carbon.
6	36	
6	36	
	36	
		120

PROTOCHLORIDE OF CARBON. (*car* + *c*).—When the above sesquichloride or perchloride of carbon is passed through a red-hot tube containing fragments of rock-crystal to increase the heated surface, it gives off a portion of chlorine, and is converted into a liquid *protochloride of carbon*. It is a limpid colourless fluid, specific gravity 1·55, and not combustible, except retained in the flame of the spirit-lamp, when it burns with a yellow flame, much smoke, and fumes of hydrochloric acid. It does not congeal at 0°; it rises in vapour at about 165°. It is insoluble in water, but soluble in alcohol, ether, and the oils. It is not affected by the acids or alkalis, nor, at common temperatures, by solutions of silver. It dissolves chlorine, iodine, sulphur, and phosphorus. It affords, when decomposed, 17 carbon + 83 chlorine; whence it may be inferred to consist of

Carbon	1	6	14·3
Chlorine	1	36	85·7
<hr/>			
Protochloride of carbon	1	42	100·0

According to Regnault the density of the vapour of this protochloride of carbon, as determined by experiment, is 5·820 (or 84 in reference to hydrogen as = 1), its formula, therefore, is probably (*2car* + *2c*), inasmuch as

	Sp. Gr.
1 volume of carbon vapour = 2 atoms	. 0·84
2 volumes of chlorine . = 2 atoms	. 4·94
<hr/>	
1 volume of vapour of protochloride of carbon } = 1 atom	. 5·78

Carbon.	Chlorine.	Protochloride of Carbon.
6	36	84
6		
	36	

DICHLORIDE OF CARBON. SUBCHLORIDE OF CARBON. (*2 car* + *c*).—This compound was accidentally obtained in Sweden, whence it was brought by Julin, and submitted to analysis by Phillips and Faraday. (*Ann. of Phil.*, N. S., i. 216, and ii. 150.) It is a solid crystalline body, volatile by heat, without decomposition, and condensing into crystals. It is insoluble in water, but soluble in alcohol, ether, and essential oils. It sinks in water. It burns with a red flame, giving off much smoke, and fumes of hydrochloric acid. Acids do not act on it. When its vapour is highly heated in a tube, chlorine is given off, and charcoal deposited. Potassium burnt with it forms chloride of potassium and liberates charcoal. Its vapour, detonated over mercury, with oxygen, formed carbonic acid and chloride of mercury: passed over hot oxide of copper, it formed a chloride of copper and carbonic acid; and over hot lime, it occasioned ignition, and produced chloride of calcium and carbonic acid. The results of its analysis by oxide of copper, show that it consists of

Carbon	2	12	25
Chlorine	1	36	75
<hr/>			
Dichloride of carbon	1	48	100

This compound was said to have been formed during the distillation of protosulphate of iron and nitre (both salts no doubt impure). All attempts at producing it by other means have failed, nor has it

been converted into either of the other chlorides. (*Phil. Trans.*, 1821, p. 392.)

CARBON AND IODINE. SESQUIODIDE OF CARBON.—This compound of carbon and iodine was first obtained by Serullas, and considered as a hydriodide of carbon. (*Ann. de Chim. et Phys.*, xx. 163, and xxii. 172.) It was subsequently examined by Mitscherlich. (*Ann. de Chim. et Phys.*, xxvii. 85.) It is produced in the form of a yellow precipitate, when a saturated solution of iodine in alcohol is mixed with a strong alcoholic solution of potassa or soda: part of the iodine combines with the potassium or sodium, and the liberated oxygen unites to the hydrogen of the alcohol to form water, whilst another part of the iodine combines with the carbon of the alcohol. Iodide of carbon is of a lemon-yellow colour, and a sweetish taste. It crystallizes in brilliant spangles; its smell somewhat resembles that of saffron: its specific gravity is nearly 2. It is not sensibly soluble in water, but dissolves in 80 times its weight of alcohol of 0·825 specific gravity at 60°, and in 25 times at 95°. One part dissolves in 7 of ether. It also dissolves in fat and volatile oils; and when its solution in oil of lemon-peel is exposed to light, it is decomposed, and charcoal and iodine are deposited. Sulphuric, sulphurous, nitric, and hydrochloric acids have no action upon it, nor has aqueous solution of chlorine; but gaseous chlorine decomposes it, and forms chloride of iodine, and a white substance, which is probably a chloride of carbon. At common temperatures it gradually evaporates when exposed to air, and at 212° volatilizes without decomposition; between 240° and 248° it enters into fusion, and is soon decomposed, giving rise to vapours of iodine and a brilliant charcoal. If moisture be present, carbonic and hydriodic acids may be formed. (*Ann. de Chim. et Phys.*, xxxvii. 85.) Serullas analyzed this compound by passing it over ignited peroxide of copper. (*Ann. de Chim. et Phys.*, xxxix. 230.) It appears to be a *sesquiodide* ($car + 1\frac{1}{2}i$), and to consist of

Carbon	1	6	3·1
Iodine	$1\frac{1}{2}$	189	96·9
Sesquiodide of carbon	1	195	100·0

PROTIODIDE OF CARBON. ($car + i$).—This compound, also mistaken by Serullas for a hydriodide (*Ann. de Chim. et Phys.*, xxv. 314), is prepared by triturating together equal parts of dry sesquiodide of carbon, and perchloride of phosphorus, and gently heating the mixture in a tubulated retort, the beak of which dips into water; a liquid passes over, which falls to the bottom of the water, and which, when carefully separated and mixed with four or five parts of sulphuric acid, is thus freed from hydrochloride of carbon, and remains at the bottom of the acid; it is ultimately separated, and having been washed with a solution of potassa, and lastly with water, is the pure *iodide of carbon*. It is a heavy, yellow liquid, of a peculiar ethereal odour and sweet taste; very little soluble in water, and not congealed at 32°. Exposed to air it gradually reddens. It does not act upon potassium; in the flame of a candle it gives out iodine. It is decomposed at a red heat when passed over peroxide of copper, and

from the produced carbonic acid, Serullas inferred (*Ann. de Chim. et Phys.*, xxxix. 231) that it consists of

Carbon	1	6	4.58
Iodine	1	126	95.42
<hr/>			
Protiodide of carbon	1	132	100.00

Recent experiments have thrown some doubt as to whether the above compounds are or are not free from hydrogen.

CARBON AND BROMINE. BROMIDE OF CARBON.—This compound was also discovered by Serullas (*Ann. de Chim. et Phys.*, xxxiv. and xxxix.), and is formed by adding two parts of bromine to one of the solid iodide of carbon, and just enough solution of potassa to occasion the disappearance of the free iodine. A liquid bromide of carbon will appear at the bottom of the solution, which is to be separated by a funnel or otherwise, but without washing with water, and allowed to stand till it has become quite clear; during this time, crystals of iodate of potassa form upon the surface; the clear fluid beneath is to be withdrawn, and put into a weak solution of potassa, for the purpose of decomposing a little protiodide of carbon formed at the same time: a little bromide is also decomposed, but that which remains is soon left in a pure state. The principal properties of this, (which is probably a *protobromide of carbon*,) and the differences between it and the liquid protiodide, are as follows: the bromide becomes solid, hard, and crystalline, at 32° , and remains solid up to 43° ; the iodide remains fluid in the lowest temperatures. The bromide gives red vapour; the iodide violet vapour, when heated in the flame of a spirit-lamp. Neither of them act upon water, but are slowly decomposed in weak alkaline solutions. (*Ann. de Chim. et Phys.*, xxxix. 225.) This compound, like the iodide, is by some suspected to contain hydrogen.

FLUORIDE OF CARBON is unknown.

CARBON AND HYDROGEN.—These elements unite in several proportions, and form many curious and important compounds, among which it is sometimes difficult to distinguish those which ought to be considered as distinct and definite combinations, from others which are probably indefinite mixtures of the former. These compounds are generally termed *hydrocarbons*, or *hydrocarburets*, and amongst them are some striking illustrations of one species of *isomerism* (from *ισος*, *equal*, and *μερος*, *part*), that is, of compounds differing, often essentially, in their physical or chemical properties, or both, and yet apparently produced by the union of the same elements bearing the same ratio to each other. Bihydrocarbon, or olefiant gas, and quadrihydrocarbon, or etherine, for instance, are in this predicament; when analyzed they are each found to consist of carbon, and hydrogen, in the same relative proportions, namely, 1 atom of carbon united to 1 atom of hydrogen; but the density of a volume of the former is to that of the latter, as 1 to 2; hence there are twice the number of simple atoms in an equivalent of etherine, that exist in an equivalent of olefiant gas; and assuming the density of hydrogen as = 1, that of olefiant gas is 14, and of etherine 28; hence we consider an atom of olefiant gas as constituted of 2 atoms of carbon, and 2 atoms of

hydrogen ($2\text{car} + 2\text{h}$), and an atom of etherine as constituted of 4 atoms of carbon, and 4 atoms of hydrogen ($4\text{car} + 4\text{h}$). Their respective volumes, equivalents, and densities, may, therefore, be represented thus; as will be obvious by referring to the following more detailed statement of their composition. Here, therefore, although the compounds are isomeric, they are represented by different equivalent numbers; but there are cases of *isomerism* in which the same elements are united in the same ratio, so as to produce compounds represented by the same equivalent number, yet essentially distinct in their chemical characters. It has been observed by Dr. Turner, that our notions of isomerism are quite consistent with our theories of chemical union, inasmuch as the same elements may be grouped, or combined in various ways, so as to give rise to compounds essentially distinct. Thus, the elements which in one form of arrangement constitute *nitrate of ammonia* ($2\text{n} + 5\text{o} + 3\text{h}$), in another constitute *nitrous oxide and water* $2(\text{n} + \text{o}) + 3(\text{h} + \text{o})$. Thus also the elements of sulphate of potassa ($\text{po} + \text{o} + (\text{s} + 3\text{o})$), may be united as expressed by the preceding formula, or as in the following ($\text{po} + \text{s} + 4\text{o}$), or they may be arranged into other aggregates.

Hydrogen.	Olefiant.	Etherine.
1	14	28

Of the compounds of CARBON and HYDROGEN, we shall here describe some of the most important of those which have the characters of distinct and definite combinations; reserving others to be noticed amongst *organic products*.

BIHYDROURET OF CARBON. DICARBURET OF HYDROGEN. LIGHT CARBURETTED HYDROGEN. FIRE-DAMP OF COAL-MINES. INFLAMMABLE AIR OF MARSHES. HEAVY INFLAMMABLE AIR. ($\text{car} + 2\text{h}$), or CH_2 .—Under these names an important variety of hydrocarbon is designated, which occasionally occurs pent up in cavities in coal-mines, (DAVY, *Phil. Trans.*, 1815,) and which is also said to be abundantly formed in stagnant pools during the spontaneous decomposition of vegetable matter, and to be procured by stirring up the fetid mud, and collecting the gas that rises in an inverted glass jar; in this state it is mixed with a little nitrogen and with carbonic acid; the latter may be separated by washing the gas in lime-water or a solution of caustic potassa. The gas procured from a *blower* in a coal-mine, after having been washed with lime-water, probably furnishes this compound in its purest state; but it does not appear that it can be produced artificially, unless it be admitted that a portion of the inflammable gas generated by the distillation of moist charcoal at a red heat, or by that of pit-coal, be similarly constituted.

Sir H. Davy found the specific gravity of this purified gas from a coal-mine to be 0.559, and compared with hydrogen as 8 to 1. 100 cubical inches weighed between 16 and 17 grains (or, according to Thomson, 18.2148 grains at the temperature of 32°), and nearly the same specific gravity is assigned to this gas (0.559) by Henry and Dalton. It is highly inflammable, burning with a yellow flame, and producing carbonic acid and water; it has a slightly disagreeable odour. It is not decomposed by electricity, but when passed through a white-hot

tube, deposits a portion of its carbon. Dry chlorine, even when aided by light, does not act upon it at common temperatures; but when the gases are moist and exposed to sunshine, a mutual action ensues; if there be excess of chlorine, carbonic and hydrochloric acid gases are produced. Passed with chlorine through a red-hot tube, or subjected to the electric spark, carbon is thrown down, and hydrochloric acid formed.

100 volumes of this gas require 200 of oxygen for perfect combustion, and the result is *water*, and 100 volumes of *carbonic acid*. 100 of carbonic acid contain 100 of oxygen, or half the quantity consumed; the remaining hundred volumes, therefore, must have combined with 200 of hydrogen to form water; hence, as

50	cubic inches of carbon vapour weigh	12.70
200	hydrogen gas	4.23
100	light carburetted hydrogen should weigh	16.93

which closely agrees with Davy's experimental result, and shows that this gas is constituted of

				Vols.	Sp. Gr.
Carbon	1	..	6	..	75.
Hydrogen	2	..	2	..	25.
Fire-damp	1		8		100.
				1.	0.554

Or,

$$\begin{array}{|c|c|} \hline \text{car} & h \\ \hline 6 & 1 \\ \hline & h \\ \hline & 1 \\ \hline \end{array} = \frac{\text{car} + 2h}{8}$$

Sir H. Davy made several experiments on the combustibility and explosive nature of this gas. He found that when 1 volume of the fire-damp was mixed with 1 of air, they burnt by the approach of a lighted taper, but did not explode; 2 of air and 3 of air to 1 of gas produced

similar results. When 4 of air and 1 of gas were exposed to a lighted candle, the mixture being in the quantity of 6 or 7 cubical inches in a narrow-necked bottle, a flame descended through the mixture, but there was no noise: 1 volume of gas inflamed with 6 of air in a similar bottle, produced a slight whistling sound: 1 of gas with 8 of air rather a louder sound: 1 with 10, 11, 12, 13, and 14, still inflamed, but the violence of combustion diminished. In 1 of gas and 15 of air, the candle burnt, without explosion, with a greatly enlarged flame; and the effect of enlarging the flame, but in a gradually diminishing ratio, was produced as far as 30 parts of air to 1 of gas. The mixture which seemed to possess the greatest explosive power was that of 7 or 8 volumes of air to 1 of gas; but the report produced by 50 cubical inches of this mixture was less than that produced by one-tenth of the quantity of a mixture of 2 parts of atmospherical air and 1 of hydrogen.

In reference to the *degree of heat* required to explode this gas mixed with its proper proportion of air, it was found that a common electrical spark would not explode 5 parts of air and 1 of the hydrocarburet, though it exploded 6 parts of air and 1 of the gas: but very strong sparks

from the discharge of a Leyden jar seemed to have the same power of exploding different mixtures of the gas as the flame of the taper. Well-burned charcoal, ignited to the strongest red-heat, did not explode any mixture of air and of the fire-damp; and a fire made of well-burned charcoal, *i. e.* charcoal that burned without flame, was blown up to whiteness by an explosive mixture containing the fire-damp, without producing its inflammation. An iron rod at the highest degree of red-heat, and at the common degree of white-heat, did not inflame explosive mixtures of the fire-damp; but, when in brilliant combustion, it produced the effect. The flame of gaseous oxide of carbon, as well as that of olefiant gas, exploded the mixtures of the fire-damp.

In respect of combustibility, then, this hydrocarburet differs most materially from the other common inflammable gases. Sir Humphry found that olefiant gas, which explodes mixed in the same proportion with air, is fired by both charcoal and iron heated to redness. Carbonic oxide, which explodes when mixed with 2 parts of air, is likewise inflammable by red-hot iron and charcoal; and hydrogen, which explodes when mixed with three-sevenths of its volume of air, takes fire at the lowest visible heat of iron and charcoal; and the case is the same with sulphuretted hydrogen. When 6 of air and 1 of the hydrocarburet were exploded over water by a strong electrical spark, the explosion was not very strong, and, at the moment of the greatest expansion, the volume of the gas did not appear to be increased more than one-half*. Nitrogen and carbonic acid mixed in different quantities with explosive mixtures of fire-damp, diminished the velocity of the inflammation. Nitrogen, when mixed in the proportion of 1 to 6 of an explosive mixture, containing 12 of air and 1 of fire-damp, deprived it of its power of explosion; when 1 part of nitrogen was mixed with 7 of an explosive mixture, only a feeble blue flame slowly passed through the mixture. One part of carbonic acid to 7 of an explosive mixture, deprived it of the power of exploding; so that its effects are more remarkable than those of nitrogen, probably, in consequence of its greater capacity for heat, and probably, likewise, of a higher conducting power connected with its greater density. These inquiries are very important, in reference to the existence of this variety of hydrocarburet, under the name of *fire-damp*, in coal-mines.

OLEFIANT GAS. HYDROGURET OF CARBON. BIHYDROCARBON. ($2CAR + 2h$.)—This gas was discovered in 1796, by the associated Dutch chemists, Bondt, Dieman, Van Troostwick, and Lawerenburg. (*Journ. de Phys.*, xiv. 178; *Ann. de Chim.*, xxi. 48.)

It is usually obtained by the decomposition of alcohol by sulphuric acid. For this purpose about two parts of the acid and 1 of alcohol (by measure) are put into a retort, and heated by a lamp; complicated changes ensue, which will be more fully explained under the article *Alcohol*; and soon after the mixture boils, the gas is evolved. It may

* This appears the expansion when the tube is very small; in larger tubes it is considerably more. The volume of the gas appears at least tripled during the explosion.

be collected over water, and should be well washed with lime-water, or solution of potassa, to abstract sulphurous and carbonic acids; it also retains a little ethereal vapour, which may be removed by agitating it with weak alcohol and afterwards with water. When thus purified its specific gravity is about '980, or compared with hydrogen as 14 to 1, and 100 cubical inches weigh about 30 grains. According to Thomson, its specific gravity is 0.9722 (the same as that of nitrogen and of carbonic oxide), and 100 cubic inches at the temperature of 32° weigh 31.8790 grains.

This gas has little odour when quite pure; it is inflammable, burning with a bright yellowish-white flame. Water absorbs about one-eighth of its volume. It is absorbed by sulphuric acid, no carbon being separated, nor sulphurous nor carbonic acid formed. In the course of several days, 1 volume of sulphuric acid absorbs between 80 and 90 of olefiant gas, and a peculiar compound results, capable of forming distinct salts. (Such compounds will be more particularly noticed under the articles *Naphthaline*, *Oil of Wine*, and *Sulphovinic Acid*.) It is unrespirable, and extinguishes flame. One part by volume requires, for perfect combustion, three of oxygen. When sulphur is heated in one volume of this gas, charcoal separates, and two volumes of sulphuretted hydrogen result. As hydrogen suffers no change of volume by combining with sulphur, it follows that olefiant gas contains two volumes of hydrogen condensed into one; hence the quantity of oxygen required for its combustion. This gas is also decomposed by heat alone, as by passing and repassing it through a red-hot tube of earthenware or metal; it then deposits its carbon, and is expanded into twice its original volume of pure hydrogen*.

When *one* volume of olefiant gas is detonated by the electric spark in a proper tube (which, on account of the violence of the explosion, should be very strong), with three volumes of oxygen, *two* volumes of carbonic acid are formed, and water is deposited: now two volumes of carbonic acid contain one volume of the vapour of carbon, and two volumes of oxygen, so that the other volume of oxygen must have condensed two volumes of hydrogen to form the water. Hence, *one* volume of olefiant gas must contain *one* volume of the vapour of carbon, and *two* volumes hydrogen: or, as

		Grains.
100	cubic inches of carbon vapour weigh	25.4
200	" hydrogen gas weigh	4.2
100	" olefiant gas should weigh	29.6

The following diagrams further illustrate the results of the combustion of one volume, or proportional, of olefiant gas with three volumes (or six proportionals) of oxygen.

* When *oil-gas*, compressed into vessels by a power equal to that of 30 atmospheres, is suddenly allowed to escape through a small aperture into the air, the *expansion* which it suffers appears to occasion in it a degree of chemical decomposition; for it deposits a black carbonaceous matter upon paper held in the current. (*Quarterly Journal*, N.S., i. 204.)

Before detonation.		After detonation.		
Olefiant Gas.	Oxygen.	Carbonic Acid.	Water.	
	Oxygen.			
	Oxygen.	$car + 2o$	Hydrogen.	Oxygen.
	Oxygen.	$car + 2o$	Hydrogen.	Oxygen.
	Oxygen.			
	Oxygen.			

Now as *one volume* of carbon vapour represents *two* equivalents, or proportionals, it is obvious, from the above statement, that olefiant gas must be composed of

	Saussure. Volumes.				Sp. Gr.	
Carbon . . . 2 . . . 12 . . . 85.7 . . . 85 . . . 1 . . .	2	12	85.7	85	1	0.843
Hydrogen . . . 2 . . . 2 . . . 14.3 . . . 15 . . . 2 . . .	2	2	14.3	15	2	0.137
Olefiant gas . . . 1 . . . 14 . . . 100.0 . . . 100 . . . 1 . . .	1	14	100.0	100	1	.980

Or, it may be thus represented:—

Carbon. 6		=	Olefiant Gas. 14
Carbon. 6			
Hydrogen. 1	Hydrogen. 1		

No compound has yet been identified (unless methylene be regarded as such) in which one atom of carbon is combined with one of hydrogen, and which would be represented by $(car + h)$, or by 0.5 volume of carbon vapour and 1 volume of hydrogen condensed into 1 volume: such a compound would have the equivalent number = 7, which would also be its specific gravity to hydrogen.

OLEFIANT GAS AND CHLORINE.—When olefiant gas is mixed with chlorine in the proportion of 1 to 2 by volume, the mixture, on inflammation, produces hydrochloric acid, and charcoal is abundantly deposited. If the gases be well mixed, and then inflamed in a tall and narrow glass jar (about 2 feet high and 4 inches in diameter), placed with its mouth upwards, the experiment is very striking; a deep-red flame gradually descends through the mixture, and a dense black cloud of carbon rises into the atmosphere; fumes of hydrochloric acid are at the same time formed, and a peculiar aromatic odour is evolved.

CHLORIDE OF HYDROCARBON. HYDROCHLORIDE OF CARBON. ($2car + 2h + c.$)—If instead of inflaming the mixture of one volume of olefiant gas and two volumes of chlorine, the gases be merely mixed, in equal volumes, over water, or in a clean and dry glass globe exhausted of air,

they act slowly upon each other, and a peculiar fluid is formed, which appears like a heavy oil: hence the term *olefiant gas*, applied to this hydrocarbon by the Dutch chemists. *Chloric ether* is the name applied to this fluid by Dr. Thomson, who, in 1810, ascertained that its component parts were chlorine and carburetted hydrogen. It was afterwards examined by MM. Robiquet and Colin (*Ann. de Chim. et Phys.*, i. and ii.), and more lately by Regnault (*Ann. de Chim. et Phys.*, lxxix. and lxxx.) The term *Hydrochloride of Carbon*, or *Hydrocarburet of Chlorine*, may properly be applied to it. It also may be formed by allowing a current of each gas to meet in a proper receiver; but there should be excess of olefiant gas, for if the chlorine be in excess, the liquid absorbs it. To purify it it should be washed in water, and then carefully distilled from fused chloride of calcium. It is transparent and colourless; its taste sweet, and somewhat acrid; its specific gravity = 1.2. It boils at 152°. According to Gay Lussac the specific gravity of its vapour is 3.44. It burns with a green flame, evolving hydrochloric acid, and largely depositing charcoal. It is decomposed when passed through a red-hot tube. As it is produced by equal volumes of chlorine and olefiant gas, it must be a compound of

					Volumes.	Sp. Gr.
Carbon	2	12	24	} Olefiant gas	1	0.98
Hydrogen	2	2	4			
Chlorine	1	36	72		1	2.47
Chloride of hydrocarbon	1	50	100		1	3.45

From Mr. Faraday's experiments, it appears that, by exposing this hydrochloride of carbon to the action of excess of chlorine, hydrochloric acid and chloride of carbon are the results. (See CHLORIDE OF CARBON.) And Mitscherlich states, that when it is exposed in the contact of water to the direct solar rays, it is converted into acetic ether and hydrochloric acid (*Lehrbuch*, 141).

Another view of the atomic constitution of this hydrochloride of carbon has been adopted by Regnault, which regards it as a combination of hydrochloric acid with the chloride of *acetyl*; the term *acetyl* being applied to a hypothetical hydrocarbon composed of $4\text{car} + 3\text{h}$, which is considered as the base of acetic acid, to which, therefore, I must here refer: but in reference to the present question it will be obvious that 2 atoms of hydrochloride of carbon contain the elements of chloride of acetyl and hydrochloric acid, for $2(2\text{car} + 2\text{h} + \text{c}) = (4\text{car} + 3\text{h}) + \text{c} + (\text{h} + \text{c})$. The origin and further application of these views will be apparent by reference to the theory of etherification, which is treated of under organic products: but they seem to me to involve discrepancies in respect to the densities of olefiant gas and of the vapour of the hydrochloride, and to confound olefiant gas with etherine or quadrihydrocarbon.

OLEFIANT GAS AND IODINE. IODIDE OF HYDROCARBON. HYDRIDIODE OF CARBON. HYDROCARBURET OF IODINE. ($2\text{car} + 2\text{h} + \text{i}$).—When iodine and olefiant gas are exposed to the action of light, they form a compound, first obtained by Faraday (*Phil. Trans.*, 1821, p. 72). Iodine and olefiant gas were put in various proportions, into retorts, and exposed to the sun's rays: after a while colourless crystals were formed, and a

partial vacuum was produced: the gas in the vessels was found to contain no hydriodic acid. The compound was purified by introducing a solution of potassa into the retort, which dissolved the free iodine; the substance was then collected, washed, and dried.

The hydriodide of carbon is a white crystalline solid, volatile without decomposition, and in some respects analogous to the hydrochloride of carbon; its taste is sweet, and its odour aromatic. It sinks in sulphuric acid of the specific gravity 1·85. It is a non-conductor of electricity. When highly heated it evolves iodine: it is not readily combustible, but when held in the flame of a spirit-lamp, burns, diminishing the flame, giving off abundance of iodine, and some fumes of hydriodic acid. It is insoluble in water, and in acid and alkaline solutions. It is soluble in alcohol and ether, and may be obtained in crystals from these solutions. The alcoholic solution is of a very sweet taste, but leaves a sharp sensation upon the tongue. Sulphuric acid does not dissolve it, but, when heated in the acid to between 300° and 400°, it is decomposed, apparently by the heat alone, and iodine and a gas (probably olefiant) are liberated. Boiling solution of potassa acts on it very slowly, but does gradually decompose it.

It was analyzed as follows, (*Quarterly Journal*, xiii.) Four grains were passed in vapour over heated copper in a green-glass tube; iodide of copper was formed, and pure olefiant gas evolved, amounting to 1·37 cubic inches, or 0·413 grains. Now 4 grains, *minus* 0·413 grains, leaves 3·587 of iodine, and 3·587 : 0·413 :: 126 : 14·3 nearly; the constitution of this compound, therefore, is analogous to that of the hydrochloride of carbon; it may be regarded as composed of

Carbon	2	12	8·63	} Olefiant gas	14
Hydrogen	2	2	1·44		
Iodine	1	126	89·93		
Iodide of hydrocarbon	1	140	100·00	1	140

OLEFIANT GAS AND BROMINE. HYDROBROMIDE OF CARBON. HYDROCARBURET OF BROMINE. ($2\text{car} + 2\text{h} + \text{b}$.)—When hydriodide of carbon is added to bromine, a hissing noise is produced, with much heat, and a bromide of iodine and fluid hydrobromide of carbon are formed. The bromide of iodine may be removed by water, and the hydrocarburet, with a slight excess of bromine, remains. It may be rendered colourless by a little alkali. If the hydriodide of carbon is in excess, but little of the hydrobromide is formed, but a subbromide of iodine.

The pure hydrobromide of carbon is colourless, heavier than water, of a penetrating ethereal odour, a very sweet taste, and very volatile. It does not change colour by exposure to air. At 22° it becomes solid, and breaks like camphor. It was formed, by Balard, by letting a few drops of bromine fall into a flask of olefiant gas. (*Ann. de Chim. et Phys.*, xxxiv.) It consists of

Carbon	2	12	13·04	} Olefiant gas	14
Hydrogen	2	2	2·18		
Bromine	1	78	84·78		
Bromide of hydrocarbon	1	92	100·00	1	92

BICARBURET OF HYDROGEN. ($6\text{ car} + 3\text{ h.}$).—For our knowledge of this combination we are indebted to Mr. Faraday. (*Phil. Trans.*, 1825, p. 440.) When certain oils are passed through red-hot tubes, as in the process for making gas for the purpose of illumination, there is at the same time a vapour produced, which, by considerable pressure, and by cold, may be reduced to a liquid state. Large quantities of this liquid were obtained at the Portable Gas-works, by subjecting the gas produced by the decomposition of whale oil, to a pressure of 30 atmospheres; this occasioned the deposition of the fluid, which was drawn off by a valve: it effervesced as it issued forth, and by the difference of refractive power, a dense transparent vapour was seen at the same time descending through the air. This effervescence immediately ceased, and the liquid was readily retained in ordinary stoppered bottles. 1000 cubical feet of good gas yielded nearly one gallon of it. It appeared as a thin light fluid, sometimes transparent and colourless, at others opalescent, being brown by transmitted, and green by reflected light; it had the odour of oil gas. Its specific gravity was 0.821: it did not congeal when cooled down to 0° ; was insoluble in water, readily soluble in alcohol, ether, and oils; slowly decomposed by nitric acid; and formed peculiar combinations with sulphuric acid, afterwards to be noticed. This fluid Mr. Faraday found to be a mixture of various bodies, differing in their degrees of volatility: to separate them, he carefully distilled successive portions of it into receivers, cooled to 0° , the receiver being changed with each rise of 10° in the retort, and the liquid retained in a state of incipient ebullition: it was thus found that the boiling-point was most constant between 176° and 190° , at which temperature considerable quantities passed over without any change in the degree. Of this rectified fluid a portion was exposed to a temperature of 0° , when part of it solidified, and being collected and dried by pressure, did not liquify till raised to 28° .

This portion constitutes the compound which we have above termed *Bicarburet of Hydrogen*. It appears as a colourless transparent liquid, having a peculiar odour like oil-gas mixed with that of bitter almonds. Its specific gravity is 0.85 at 60° . When cooled to a little below 32° , it solidifies, and contracts considerably on congealing. It does not conduct electricity; evaporates when exposed to air; boils at 186° . The specific gravity of its vapour is 2.77, or compared with hydrogen as 39 to 1. 100 cubical inches, therefore, at mean temperature and pressure, would weigh about 85 grains. It is very slightly soluble in water, but readily soluble in alcohol and ether, and in oils. It burns with a bright flame and much smoke, and when put into oxygen furnishes sufficient vapour to form a detonating mixture. Passed through a red-hot tube, it is resolved into carbon and carburetted hydrogen gas. Placed in the sunshine in chlorine, heat is evolved, hydrochloric acid formed, and a solid and liquid are produced, which appear to be compounds of chlorine, carbon, and hydrogen. Iodine does not act upon it, but dissolves it in small quantity, forming a crimson solution. Potassium exerts no action upon it at a temperature of 186° . Neither alkalis nor their carbonates act upon it. Nitric acid occasions in it little other change than the formation of a minute portion of hydrocyanic acid. Sulphuric acid added to it over mercury, exerted a moderate action; no heat was evolved, no blackening

took place, no sulphurous acid was formed, but the acid became of a light-yellow colour, and a portion of a clear colourless fluid floated, which appeared to be a product of the action, and which was not altered by water, and solidified at 34° , being then white and crystallized.

Mr. Faraday's attention was next directed to the *composition* of the substance: he decomposed it by passing its vapour over heated oxide of copper, by which it was resolved into carbonic acid and water; and a careful determination of their weights gave (as the mean of several experiments) 1 hydrogen and 11.576 carbon, as its components. Several other experiments led to the conclusion, that in this substance the carbon and the hydrogen are in the mutual ratio of 12 to 1. But on examining the volume of oxygen requisite for the combustion of this substance, it was found that 100 volumes of its vapour required 750 of oxygen, and that the result was water, and 600 volumes of carbonic acid; so that to form the water 150 volumes of oxygen must have combined with 300 of hydrogen, and the remaining 600 volumes must have united to 300 volumes of carbon vapour to form 600 of carbonic acid. Hence, as

300 cubic inches of carbon vapour weigh	Grains.
300 " hydrogen gas	76.2
100 " vapour of this bicarburet should weigh	82.6

we must accordingly conclude, that although the ratio of the carbon to the hydrogen, in this compound, is as 12 to 1, it, in fact, consists of

	Atoms.			Vols.	
Carbon	6	36	92.31	3	2.529
Hydrogen	3	3	7.69	3	0.197
Bicarburet of hydrogen	1	39	100.00	1	2.726

Or, it may thus be represented:—

Carbon. 6	Hydrogen.
Carbon. 6	1
Carbon. 6	Hydrogen.
Carbon. 6	1
Carbon. 6	Hydrogen.
Carbon.	1

= Vapour of
the
Bicarburet.
39

LIQUID HYDROCARBURET.—In examining the liquid remaining after the separation at 0° of the above crystalline solid, it was found to exhibit peculiarities which seem to identify it as a peculiar and definite compound; and from such experiments as were made upon it, it is extremely probable that it consists of one proportional of each of its components, but in what state of condensation has not been determined.

QUADRIHYDROCARBURET. ETHERINE. ($4\text{ car} + 4\text{ h.}$)—It has already been stated, that a portion of the original oil-gas liquor is *volatile at common temperatures*; at the heat of the hand it passes off in vapour, and

may be collected as a gas over mercury. It burns with a brilliant flame: its specific gravity to that of hydrogen is as 28 to 1; to that of common air as 1.963 to 1; and 100 cubic inches weigh 59.3 grains. It condenses into a liquid when cooled to 0°, and enclosed in this state in a tube of known capacity, and hermetically sealed, the bulk of a given weight of it at common temperatures was ascertained: this, compared with water, gave its specific gravity as 0.627 at 54°; so that among solids or liquids it is the lightest body known. It scarcely dissolves in water, but readily in alcohol, and the solution effervesces from the escape of vapour when water is added. It is abundantly condensed by sulphuric acid. One volume of the acid condenses above 100 volumes of the vapour, producing great heat, but no sulphurous acid. The solution is dark-coloured, has a peculiar odour, and evolves no gas upon dilution. By detonation with oxygen, it was found that 1 volume of the vapour required 6 volumes of oxygen for perfect combustion, giving rise to 4 volumes of carbonic acid. The remaining 2 volumes of oxygen must have combined with 4 of hydrogen to form water. Upon which view, 4 volumes or proportionals of hydrogen = 4, are combined with two volumes of gaseous carbon, or 4 proportionals (6×4) = 24, to form 1 volume of the vapour, the specific gravity of which, compared with hydrogen, would be 28, which is also its equivalent number; or if

200 cubic inches of carbon vapour weigh	50.8
400 " hydrogen gas "	8.4
100 " etherine vapour should weigh	59.2

which closely approximates to the experimental result, so that the volume of etherine and its components may be represented thus:

Carbon. 6		Carbon. 6		=	<div>Etherine. 28</div>
Carbon. 6		Carbon. 6			
Hydrogen. 1	Hydrogen. 1	Hydrogen. 1	Hydrogen. 1		

and it consists of

	Atoms.			Vols.		Sp. Gr.
Carbon	4	24	85.71	2		1.686
Hydrogen	4	4	14.29	4		0.274
<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
Etherine	1	28	100.00	1		1.960

CHLORIDE OF ETHERINE.—As the relative proportions of the elements in this compound are the same as in olefiant gas, it became interesting to ascertain whether chlorine had the same action upon it. Chlorine and the vapour were therefore mixed in an exhausted retort, heat was evolved, and a liquid resembling hydrochloride of carbon formed; but it could not be identified with it, inasmuch as it consisted of nearly equal volumes of the vapour and of chlorine; and, therefore, contained twice as much carbon and hydrogen. It was, therefore, treated with excess of chlorine in sunlight; hydrochloric acid was formed, and chlorine absorbed; a peculiar fluid was also formed, consisting of hydrogen, chlorine, and carbon, but no

chloride of carbon. It seems not improbable that a compound of etherine and chlorine corresponding with that of olefiant gas and chlorine (or as some have called it "the Dutch liquor,") may exist, and this would agree with Regnault's formula, $(4\text{ car} + 4\text{ h} + 2\text{ c.})$ The elements of this chloride of etherine would be perfectly consistent with those of a combination of hydrochloric acid, with chloride of acetyl; in which case etherine might be represented as a hydruret of acetyl, or as $(4\text{ car} + 3\text{ h}) + \text{h}$, which, when exposed to chlorine, absorbs 2 volumes or equivalents; so that a chloride of acetyl and hydrochloric acid are formed, giving rise to $(4\text{ car} + 3\text{ h} + \text{c}) + (\text{h} + \text{c.})$ In other words, etherine, losing an atom of hydrogen, becomes acetyl, and if that atom of hydrogen be replaced by an atom of chlorine, chloride of acetyl is formed; if the displaced atom of hydrogen also combine with an atom of chlorine, it produces an atom of hydrochloric acid, which, combined with the chloride of acetyl, produces the hydrochlorate of chloride of acetyl, the elements of which are those of a bichloride of etherine. Regnault further finds, that when the hydrochlorate of chloride of acetyl is subjected to the further action of a stream of chlorine, another atom of hydrogen is carried off as hydrochloric acid, and an atom of chlorine left in its place; thus $(4\text{ car} + 3\text{ h} + \text{c}) + (\text{h} + \text{c})$ becomes $(4\text{ car} + 2\text{ h} + 2\text{ c}) + (\text{h} + \text{c})$, and by the continuous action of chlorine the whole of the hydrogen is ultimately carried off as hydrochloric acid, and perchloride of carbon remains.

Mr. Faraday's researches, in reference to the various forms of hydrocarbon, established a new and important fact in chemistry, which is, that substances may exactly resemble each other in the relative proportions of their constituents, and yet, in consequence of peculiarities in their atomic arrangement, exhibit perfectly distinct physical and chemical properties, presenting, as already remarked, a curious and interesting modification of isomerism. Thus, in etherine and in olefiant gas, the carbon and hydrogen are in the ratio of 6 to 1; but, in the former, the elements are united in the proportion of 24 to 4, and in the latter of 12 to 2. It has been observed by Dr. Turner, that this peculiarity is explicable on the supposition that the ultimate elements of such compounds are differently disposed. "It is to be presumed that the smallest possible particle of olefiant gas contains 2 atoms of carbon, and 2 of hydrogen; and that, in like manner, an integrant particle of etherine contains 4 atoms of each element. Neither of these substances could, I conceive, be formed by the direct union of a single atom of carbon and a single atom of hydrogen. If a combination of the kind were to occur, a new compound, different from any known at present, would be the result."

In respect to the nomenclature applicable in such cases there is obviously much difficulty. The compound of 2 atoms of carbon and 2 of hydrogen might be called *bihydrocarbon*, but the designation *olefiant gas*, however objectionable, is still generally retained. For the compound of 4 atoms and 4, the term *quadrocarburetted hydrogen* has been proposed, but that would rather imply it to consist of 4 atoms of carbon and 1 of hydrogen, than of 4 and 4; the term *quadrihydrocarbon* or *quadrihydrocarburet* has, therefore, been substituted; but perhaps *etherine* is less objectionable, implying its existence as an hypothetical base of *ether*, under which we shall again have to advert to it.

TERHYDROCARBON. SUPEROLEFIANT GAS. ($3\text{car} + 3\text{h.}$)—It seems probable that a hydrocarbon, the vapour of which contains in 1 volume 3 atoms of hydrogen and 3 of carbon, is occasionally produced during the destructive distillation of oil; and Dr. Henry (*Phil. Trans.*, 1821, p. 156) adverts to such a compound, discovered in oil gas by Mr. Dalton. Dr. Thomson describes it under the name of *tritocarbonyhydrogen*, but till some definite mode of obtaining it has been pointed out, and its properties experimentally ascertained, its distinct existence must remain doubtful.

NAPHTHA. ($6\text{car} + 5\text{h.}$)—This term is generally applied to a peculiar liquid hydrocarbon, which is both a natural and artificial product. Natural naphtha is obtained in considerable quantity at Baku, near Derbent, on the north-west shore of the Caspian Sea. The soil is a clayey marl, and so impregnated with naphtha, that, when turned up to the depth of a few inches, it will inflame on the application of a lighted candle; in this soil pits are sunk, in which the naphtha collects in considerable quantities. The purest European naphtha comes from Monte Ciaro, near Piacenza, in Italy: this hill consists of horizontal beds of argillite, in which pits are sunk till the water comes in, upon the surface of which the naphtha oozes and collects, and is occasionally skimmed off. An inferior kind is produced at Monte Festino, near Modena, in the vicinity of which subterranean fires often break out. A similar liquid may be obtained by the distillation of *petroleum*, or mineral tar, a substance which will be described among Bitumens.

Under the name of *coal-oil*, or *coal-naphtha*, a product closely resembling the former is known in gas-works; it is one of the results of the destructive distillation of pit-coal, some of the varieties of which yield it in large quantities; it is extremely volatile, and therefore generally passes on with the gas to the remoter parts of the condensing-apparatus, and often collects in large quantities in the gas-meters and gasometer-tanks, and even in the first branches of the mains, from the syphons of which it is often drawn off. When it is purified by distillation it is a colourless limpid liquid.

The properties of naphtha differ somewhat according to the sources whence it is obtained, but when carefully rectified or purified by repeated distillation with water, it appears to possess the same leading characters and composition, whatever be its source: indeed, it is extremely probable that natural and artificial naphtha are of one and the same origin, the former being derived from volcanic, the latter from ordinary distillation. The specific gravity of the purest Persian and Italian naphtha, varies from $\cdot 750$ to $\cdot 760$. But of the coal naphtha, from $\cdot 820$ to $\cdot 860$. The odour of the former is strong, bituminous, but not disagreeable; that of the latter, penetrating and unpleasant. It does not congeal at 0° . Upon the approximation of a flaming body, naphtha takes fire and burns with a voluminous, and very sooty, and difficultly-extinguishable flame. It communicates odour to water and to common alcohol; it dissolves in absolute alcohol, and in ether, petroleum, and oils. Caustic potash forms an imperfect soapy compound with it. Sulphuric and nitric acid slowly modify and decompose it. When pure, it is not acted on by potassium or sodium, and is, therefore, used to preserve those metals from oxidation. The boiling-point of naphtha is variously stated. It generally begins to boil

at about 160° , and the thermometer gradually rises to about 200° , where it continues some time, and then again rises to above 300° . Dr. Thomson states the boiling point of Persian naphtha, to be 320° to 352° . The density of its vapour is about 2.8. It dissolves the greater number of the essential oils, and the resins, and a little phosphorus and sulphur, and corrodes cork; it is remarkable for its property of dissolving caoutchouc, which first swells up, and then gradually gelatinizes, when digested in it with the aid of a gentle heat: in this pulpy state it is used to render various articles of clothing *water-proof*; the goods are stretched out, and varnished over with it, and then their varnished sides are applied to each other, and made to adhere by powerful pressure, so as to form a compound fabric or texture: the manufacture is completed, and the solvent driven off, by exposure to a moderate heat. This important and well-known application of the solution of caoutchouc in naphtha, or coal-oil, was first suggested by Mr. Macintosh, of Glasgow. Among other sources of naphtha, or at least of a liquid hydrocarbon closely resembling it in all its leading properties, we may enumerate caoutchouc itself, which yields it by destructive distillation. (See *Caoutchouc*.) The ultimate composition of naphtha has been variously stated, probably from the difficulty of obtaining it in one definite state, but all analysts agree in representing it as a true hydrocarbon. According to Dumas, a definite compound, having all the characteristic properties of naphtha, is obtained by depriving *spirit of turpentine* of its oxygen, by the action of potassium, and then subjecting it to careful distillation. (*Ann. de Ch. et Ph.*, L. 238.) When the vapour of these hydrocarbons has the density of 2.87, one volume of it may be regarded as containing three volumes of carbon vapour, and five volumes of hydrogen, and as

300 cubic inches of carbon vapour weigh	Grains.
500 " hydrogen gas weigh	78.9
100 " naphtha vapour should weigh	10.6
	89.5

Hence naphtha, or a hydrocarbon so constituted, would consist of

	Atoms.			Vols.	Sp. Gr.
Carbon	6	36	87.80	3	2.53
Hydrogen	5	5	12.20	5	0.34
	1	41	100.00	1	2.87

Or, by volume,

Carbon.	Carbon.	Carbon.		
6	6	6		
Carbon.	Carbon.	Carbon.		
6	6	6		
Hydrogen.	Hydrogen.	Hydrogen.	Hydrogen.	Hydrogen.
1	1	1	1	1

=
 Naphtha
Vapour.
41

By subjecting coal-naphtha to the action of chlorine, Laurent (*Ann. de Ch. et Ph.*, Lxiii. 27) has obtained two acid compounds, to which he has given the names of *chlorophenismic* and *chlorophenesic acids*. The former is a white solid, constituted in its anhydrous state by ($^{12} \text{car} + 3 \text{h} + 2 \text{o} + 3 \text{c.}$) The latter is represented by ($^{12} \text{car} + 4 \text{h} + 2 \text{o} + 2 \text{c.}$)

NAPHTHALIN. ($10\text{ car} + 4\text{ h.}$)—This name was first given by Dr. Kid (*Phil. Trans.*, 1821, p. 209), to a concrete crystalline substance found among the products of the coal-gas manufacture; it may be obtained by subjecting coal-tar to distillation; it passes over after the naphtha or coal-oil: when any of the varieties of the tar are so distilled that their vapour may be exposed to a high temperature, more or less naphthalin is formed. I believe that I first pointed it out as a binary compound of carbon and hydrogen, in 1819. (*Quar. Journ.*, viii. 287.) It was afterwards examined by Mr. Chamberlain. (*Ann. of Philos.*, xix.) It is generally first obtained in translucent flakes of a red or brown colour. By slow sublimation with a portion of powdered charcoal, it may be obtained colourless, and nearly inodorous; but when heated, it exhales a peculiar faint odour, which has been compared to that of the flower of the narcissus. Its taste is slightly aromatic; it is heavier than water, unctuous to the touch, and slowly evaporates at common temperatures. It fuses at about 200° , and crystallizes as it cools; at 400° it boils and distils over, with little change. When inflamed, it throws off a singularly large quantity of black smoke, which diffuses itself in light films of carbon through the air. It is insoluble in cold, and very slightly soluble in boiling water; alcohol, ether, the oils, and naphtha, dissolve it abundantly. The alkalis have no action on naphthalin: when long boiled in nitric acid, it is slowly altered, and a part of the acid decomposed: hot hydrochloric acid dissolves it very sparingly; acetic and oxalic acids more copiously: sulphuric acid dissolves and combines with it.

The proportions of carbon and hydrogen which constitute naphthalin, were first determined by Faraday, and his results subsequently confirmed by Liebig, Wöhler, and Laurent. The specific gravity of its vapour is 4.49, or compared with hydrogen as 64 to 1, so that 100 cubic inches should weigh 135 grains; assuming therefore 100 volumes of it to consist of 500 of carbon vapour, and 400 of hydrogen,

	Grains.
500 cubic inches of carbon vapour	= 127.0
400 " hydrogen gas	= 8.5
100 " naphthalin vapour	= 135.5

Hence the atomic composition of naphthalin stands as follows:—

	Atoms.			Vols.	Sp. Gr.
Carbon . . .	10 . . .	60 . . .	93.75 . . .	5 . . .	4.213
Hydrogen . .	4 . . .	4 . . .	6.25 . . .	4 . . .	0.277
Naphthalin	1	64	100.00	1	4.490

Or, by volume,

Carbon. 6	Carbon. 6	Carbon. 6	Carbon. 6	Carbon. 6
Carbon. 6	Carbon. 6	Carbon. 6	Carbon. 6	Carbon. 6
Hydrogen. 1	Hydrogen. 1	Hydrogen. 1	Hydrogen. 1	

Naphthalin
Vapour.

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NAPHTHALIN AND CHLORINE. CHLORIDE OF NAPHTHALIN.—The mutual action of chlorine and naphthalin has been examined by M. Laurent (*Ann. de Chim. et Phys.*, lii. 275). When chlorine is passed over naphthalin, heat is evolved, hydrochloric acid formed, and a semifluid compound remains, consisting of a solid and liquid chloride; the latter may be removed by cold ether. The *solid chloride* is insoluble in water, sparingly soluble in hot alcohol, and more soluble in boiling ether, from which it separates on cooling in transparent rhomboids. It fuses at 320° and in close vessels boils and is decomposed; but when carefully heated in a current of air, it may be volatilized without decomposition. It is not readily acted on either by acids or alkalis.

The *liquid chloride*, obtained by the evaporation of its ethereal solution, is yellow; insoluble in, and heavier than water: it is soluble in alcohol and ether, and may be distilled without decomposition. Analysis shows, that both these compounds contain chlorine in combination with a hydrocarbon, differing in composition from naphthalin; hence the term chloride of *naphthalin* is not quite appropriately applied to it. The exact proportion of its components has not been ascertained with precision.

NAPHTHALIN AND NITRIC ACID.—Two compounds of nitric acid and naphthalin have also been described by Laurent (*Ann. de Ch. et Ph.*, lix. 381), which he has distinguished as *nitronaphthalase* and *nitronaphthalese*. By distilling nitronaphthalase with lime he obtained a solid yellow sublimate, which he considers as the basis of that compound, and which he has called *naphthalase*.

NAPHTHALIN AND SULPHURIC ACID. SULPHONAPHTHALIN. SULPHONAPHTHALIC ACID. ($20 \text{ CAR} + 8 \text{ H} + 2 \text{ S}'$).—The action of sulphuric acid on naphthalin has been investigated by Faraday (*Phil. Trans.*, 1826). He found that, like several other hydrocarbons, it combined with that acid, and produced a peculiar acid body, which he called *Sulphonaphthalic acid*. He obtained it pure, by the following process: Naphthaline was fused with half its weight of sulphuric acid, which, on cooling, formed a red crystalline compound, soluble in water; carbonate of baryta was added to its solution, by which sulphate and sulphonaphthalate of baryta were formed; the former insoluble, but the latter soluble; its solution was filtered off, and sulphuric acid added to it sufficient to precipitate the baryta. An aqueous solution of sulphonaphthalic acid was thus obtained, of a bitter acid taste, and powerfully reddening litmus: concentrated by evaporation it became brown, thick, and, ultimately, solid and very deliquescent. By renewed heat it melted and charred, but did not flame, and ultimately gave sulphuric and sulphurous acid vapours, and left charcoal. Another portion of the acid was evaporated under an exhausted receiver, including a vessel of sulphuric acid. In some hours it became a white soft solid, apparently dry, and after a longer period was hard and brittle. In this state it was deliquescent in the air, but might be preserved unaltered in a close vessel. Its taste was bitter, acid, and metallic: when heated to 212° it melted, and crystallized and solidified as it cooled: more highly heated, water passed off, and it assumed a red tint, becoming probably anhydrous; further heated, it became brown and black, and naphthaline, sulphurous acid, and charcoal

were evolved. This acid dissolves in water, alcohol, and oils. Its aqueous solution forms neutral salts with bases, all of which are soluble in water, most of them in alcohol, and all combustible, leaving sulphates or sulphurets, according to circumstances.

To determine the composition of this acid, and its equivalent number, its neutral salt with baryta was chiefly experimented upon: and the following appear to be the relative proportions of its elements:—

Baryta	1	77	27.0
Sulphuric acid	2	80	28.1
Carbon	20	120	42.1
Hydrogen	8	8	2.8
<hr/>			
Sulphonaphthalate of baryta 1		285	100.0

We have, therefore, the following composition of the sulphonaphthalic acid:—

Carbon	20	120	57.8
Hydrogen	8	8	3.8
Sulphuric acid	2	80	38.4
<hr/>			
Sulphonaphthalic acid	1	208	100.0

Of the two proportionals, therefore, of sulphuric acid, one is, as it were, saturated by the hydrocarbon, for it only combines with 77 of baryta, which will be found to be the equivalent of one proportional of that base. This curious property of hydrocarbon, indicating its capability of uniting to an acid, saturating it, and performing, as it were, the part of a basis, has been more extensively inquired into and illustrated by Mr. Hennell: his experiments relate chiefly to certain combinations concerned and developed in the formation of ether, under which article the details will be given.

PARANAPHTHALINE.—Under this term Dumas and Laurent (*Ann. de Chim. et Phys.*, L. 187) have described a hydrocarbon closely resembling naphthaline in all its essential properties, but yielding a vapour having the density of 6.78, whence they infer that it consists of 15 atoms of carbon and 4 of hydrogen. Paranaphthaline is less volatile than naphthaline, and, therefore, when coal-tar is distilled, it is among the latter of its products. According to Reichenbach (*POGGEND., Ann.*, xxviii. 484), paranaphthaline is a mixture of naphthaline and another definite hydrocarbon, which he terms *paraffine*, and which we shall describe amongst organic products.

IDRIALINE.—This term is applied by Dumas to a native hydrocarbon, found in the mercury-mine of Idria, in Carniola, and which appears to be very analogous to naphthaline: it is said to consist of 3 atoms of carbon and 1 of hydrogen. (*Ann. de Chim. et Phys.*, L. 193.)

GAS ILLUMINATION: COAL-GAS.—Mixtures of the hydrocarbons now described, and of some other gaseous compounds, are abundantly produced during the destructive distillation of coal and oil, and of a variety of other vegetable and animal substances; and the gases thus obtained are employed for the purposes of illumination, as economical substitutes for tallow, oil, &c. The destructive distillation of pit-coal is a process carried

on upon a very extensive scale in several public and many private establishments. The coal is placed in oblong cast-iron cylinders, or *retorts*, which are ranged in furnaces, to keep them at a red-heat, and all the volatile products are conveyed by a common tube into a *condensing vessel*, kept cold by immersion in water; and in which the water, tar, ammoniacal, and other condensible vapours, are retained: the gaseous products consist principally of varieties of carburetted hydrogen, with more or less sulphuretted hydrogen, and carbonic oxide, and acid: these are passed through or over hydrate of lime, or through a mixture of quicklime and water*, in vessels called *purifiers*, by which the sulphuretted hydrogen and carbonic acid gases are absorbed, and the carburetted hydrogen gases transmitted sufficiently pure for use into *gasometers*, whence the pipes issue for the supply of streets, houses, &c. The coke remaining in the retorts is of a very good quality†.

The specific gravity of purified coal-gas is liable to much variation: sometimes it falls below 0.450, and at others exceeds 0.650. These differences are partly referable to the nature of the coal, but chiefly to the manner in which the process of distillation is conducted, as to duration, and temperature: it has already been remarked, that when the varieties of hydrocarbon are passed through highly-heated tubes, they are more or less perfectly decomposed into carbon and hydrogen: hence the gas which is obtained at a high temperature, or which, after its formation, has been in contact with red-hot surfaces, is apt to be partly decomposed; it is thus increased in bulk, but diminished in specific gravity, and in illuminating power; hence, too, analysis detects in coal-gas, more or less

* Mr. Parker, of Liverpool (*Phil. Mag.* vol. iii. p. 292), has proposed to pass the gas, as it comes from the coal-retorts, through red-hot iron tubes, by which the contaminating gases and vapours are further decomposed, and the quantity of useful gas much increased. This suggestion, if it succeeded, would greatly diminish the quantity of tar; but as carburetted hydrogen is decomposed at a red heat, it would, probably, tend to diminish the illuminating power of the gas, though it would increase its quantity. The *purification* of coal-gas is a subject of the utmost importance, especially as relates to perfectly freeing it from sulphuretted hydrogen, which if present produces *sulphurous acid* during combustion, and is, therefore, highly noxious; in the case of the escape of unburnt gas, sulphuretted hydrogen is an equal evil; it is fetid and unwholesome, and it causes the immediate tarnishing of silver and other metals: its presence is fortunately very easily detected by a piece of paper moistened with a solution of sugar of lead, and no gas should be allowed to be burned, which *blackens* that test. Coal-gas, however, though free from sulphuretted hydrogen, occasionally pro-

duces a little sulphurous acid when burned, and in such cases I suspect the presence of the vapour of sulphuret of carbon. Ammonia or some ammoniacal compound is also often found in coal-gas even after it has been deprived of all sulphur: its presence is very injurious to copper tubes and brass stop-cocks. It has been proposed to free the gas from this contamination by passing it through dilute sulphuric acid, or through a solution of alum.

† The following is, I believe, a correct account of the manufacture of gas for London and the suburbs on the 1st of January, 1835. 30 gas-works employing a capital of 2,200,000*l.* and deriving a yearly rental of about 400,000*l.*, using annually about 112,000 tons of coal, which produce about 1000 millions cubic feet of gas. There are in these works about 130 gas-holders, the united contents of which exceed 3,500,000 cubic feet; they supply about 120,000 lamps. During the longest nights, about 4,910,000 cubic feet of gas are consumed each night, for the production of which about 550 tons of coals are daily carbonized.

uncombined hydrogen. The best kind of coal for distillation is that which contains most bitumen and least sulphur. The chaldron should yield about 12000 cubical feet of purified gas, of which each Argand's burner, equal to six wax-candles, may be considered as consuming from four to five cubical feet per hour.

OIL GAS.—Some years ago, Messrs. J. and P. Taylor invented an apparatus for the conversion of oil into gas. It consists of a furnace with a contorted iron tube containing fragments of brick or coke, passing through it, into which, when red-hot, the oil is suffered to drop; it is decomposed, and converted almost entirely into charcoal, which is deposited in the tube, and into a mixture of carburetted hydrogen gases and vapours, of which from two to three cubic feet may be regarded as equivalent to five or six of coal-gas, for the production of light. (*Quarterly Journal*, vol. viii.) The commonest whale-oil, or even pilchard-dregs, quite unfit for burning in the usual way, afford abundance of excellent gas, requiring no other purification than passing through a refrigerator, to free it of its more condensable vapours*. A gallon of whale-oil affords about 90 cubical feet of gas of an average specific gravity of 0.900, and an Argand burner, equal to seven candles, consumes a cubical foot and a half per hour. If its specific gravity exceed 0.900, it may be considered as containing too large a proportion of the heavier hydrocarbons, by which the bulk of the produce is much diminished, which are apt to condense in the pipes and gasometer, and which also occasion a fuliginous deposit during the consumption of the gas in ordinary burners.

RESIN GAS.—In consequence of the high and generally fluctuating price of oil, it became an important object to obtain a gas, of equal brilliancy and purity to that which it affords, from materials at once cheaper and less liable to fluctuations of value; and with this view, attempts were made to decompose resin, in the apparatus above described. For this purpose melted resin was substituted for the oil; but the exit-pipes, by which the gas flowed off, soon became choked with a thick bituminous substance, which stopped the process; and the product of gas was small, and of inferior quality. Mr. Daniell overcame this difficulty, by the invention of an apparatus, for which he obtained a patent. The exit-pipe of the oil-gas apparatus rose from the upper part of the retort, and was purposely carried to a considerable height, that the volatile oil, which was condensed during the process, might flow back and add to the product of gas by its decomposition. It was the return of the volatile oil from resin, which choked up the pipes when that substance was employed; and Mr. Daniell, observing this, led the exit-pipe from the *under* part of the retort into the hydraulic main, so that the return of any condensed vapour was rendered impossible. His mode of treating the resin is to dissolve, with the assistance of a gentle heat, about 8 lbs. in a gallon of the essential oil, which is plentifully formed during the decomposition of oil for making gas, or of resin itself. This solution is allowed to trickle into

* Mr. G. Lowe, of the Chartered Gas Company, informs me that the gas from oil and resin not unfrequently contains 10 per cent. of carbonic acid, the effect of which on the illuminating power of the gas must be very detrimental.

the heated retort half filled with coke. A small diaphragm, just behind the exit-pipe, and filling half the diameter of the retort, prevents any of the liquid flowing into the hydraulic main. When the process is properly conducted, about 1000 to 1200 cubic feet of gas are obtained from the cwt. of resin, and rather more than the original quantity of volatile oil is condensed, which is again employed for the solution. It is necessary to add a small quantity of lime to the essential oil, to neutralize a little acetic acid, which is formed during the process. The apparatus works perfectly free from all obstruction. The gas thus formed is equal in quality to oil-gas of 100 cubic feet to the gallon. Its average specific gravity is 0.850; it requires no purification; and its smell is rather resinous, and not nearly so offensive as that of either oil or coal-gas. Two cubic feet are equal in illuminating power to above five of the common coal-gas, and the expense of the material from which it is made, is not above one-third of the expense of oil. The sources of supply are as inexhaustible, and more generally distributed, than those of coal; and the forests of America, France, Spain, and Italy, yield the turpentine in quantities only limited by the demand. Many large towns in this country, in America, France, Holland, and the Netherlands, at one time adopted the use of this gas, but the late improvements in the production of coal-gas have I believe led to the abandonment both of it and of oil-gas. The elegance and simplicity, however, of the manufacture, and the comparatively small capital required for the erection of the works, may, in some situations, give it a preference.

COMPOSITION AND ANALYSIS OF THE GASES USED FOR ILLUMINATION.—

Dr. Henry's researches are the most important in reference to the philosophy of the art of gas-illumination (NICHOLSON'S *Journal*, 1805; *Phil. Trans.*, 1808 and 1821, and 1824), and much interesting matter connected with the subject will be found in an essay by Dr. Turner and Dr. Christison (*Edin. Phil. Jour.*, 1825). The treatises of Mr. Accum and of Mr. Peckston contain an account of the apparatus, with details as to its construction and expense, together with much useful practical information.

The analysis of a mixture of hydrogen with carbonic oxide, carbonic acid, and hydrocarbon, often requires to be performed in investigations relating to the gases used for illumination; it may be approximately effected as follows: A hundred measures of the gas are introduced into a graduated tube, and the carbonic acid absorbed by a solution of potassa; the remaining gas is then transferred to thrice its volume of chlorine of known purity, standing over water in a tube of about half an inch diameter, and carefully excluded from the solar rays; after 24 hours the hydrocarbons and the excess of chlorine will have been absorbed, especially after a little agitation, and the remaining gas, if it consist of carbonic oxide and hydrogen only, may be analyzed by detonation with oxygen in excess; the measure of carbonic acid formed being equal to that of the original carbonic oxide. This proceeding depends upon the non-formation of chlorocarbonic acid in a mixture of carbonic oxide and chlorine in the contact of water, and out of the direct agency of the solar rays. Such mixture I have kept several days, occasionally renewing the chlorine as it became absorbed by the water, and have not observed any diminution in the bulk of the carbonic

oxide. In these cases it is necessary to ascertain the purity of the chlorine by its absorption by water, and to take care that no hydrocarbon has escaped its action.

But in consequence of the presence of other compounds of carbon and hydrogen, and of those singular vapours discovered by Mr. Faraday, in coal, and especially in oil and resin gases, the accurate analysis of these complicated products becomes a problem of some difficulty. Dr. Henry's papers (in the *Phil. Trans.*, for the years 1818, 1820, and 1824, and in the *Annals of Phil.*, vol. xv.,) contain details upon the subject, which the student should carefully consult. The removal of the hydrocarburetted vapours from these gases may, as Mr. Faraday has shown (*Phil. Trans.*, 1825, page 461), be accurately effected by the agency of sulphuric acid: this also absorbs olefiant gas, but much less rapidly than the vaporous compounds; and if the gas under examination be diluted with three or four times its bulk of common air or of hydrogen, and excluded from the sunshine, the absorption of olefiant gas by the acid will be prevented. The hydrocarburetted vapours may also be removed by subjecting the gas to the action of olive-oil already saturated with olefiant gas.

As far as concerns the comparative value of different hydrocarburetted gases for the purpose of illumination, it seems evident, from Dr. Henry's experience, that, whatever be their source or composition, it may be most accurately determined by the quantity of oxygen required to saturate equal volumes. In other words, the illuminating powers of the different gases will be proportioned to the number of volumes of gaseous carbon condensed into one volume of the gas; and of these the oxygen consumed, and the carbonic acid produced, afford an accurate measure. (HENRY'S *Elements*, 1826, vol. i. 432.) "If 100 volumes, for instance, of one gas, require for perfect combustion 100 volumes of oxygen, and 100 volumes of another gas take 200 of oxygen, the value of the second will be double that of the first. Specific gravity, though a guide to a certain extent, is not a sufficient one; for the weight of a gas may be owing to a large proportion of carbonic oxide, which only gives out a very small quantity of light. Photometrical experiments also appear to me to require greater perfection in the instruments that have been invented for that purpose, before we can implicitly trust to results obtained by their means: but there can be no fallacy in the combustion of these gases by oxygen, if conducted with ordinary care, and especially if in each instance an average be taken of two or three trials, which need not occupy more than a few minutes. Nor can it admit of doubt, that, other circumstances being equal, the brilliancy of light evolved by the combustion of gases which are constituted of purely inflammable matter, will bear a proportion to their densities, perhaps even a greater proportion than one strictly arithmetical; because, while, by the combustion of denser gases, a higher temperature is produced, the cooling agencies remain the same. It is probable, therefore, that of two gases composed of the same ingredients, that which has a double density will afford somewhat more than a double quantity of light."

ECONOMY OF GAS-ILLUMINATION.—The economy of gas-illumination may be judged of by examining the value of the products of distillation

of a chaldron of coals, the average cost of which may be considered as 25s. It should afford—

	£	s.	d.
1½ chaldron of coke, at 13s.	0	16	3
24 gallons of tar, ammoniacal liquor, and other products, at 1d.	0	2	0
12000 cubic feet of gas, at 10s. per 1000 C. F.	6	0	0
	£6	18	3

These products are taken nearly at their lowest value, but they afford ample grounds for showing the advantage of gas-illumination, not merely for public purposes, but also in private establishments. It appears that where about one hundred lights are required, a coal-gas apparatus will be found profitable.

The cost of a lamp, fed by gas, and giving the light of seven candles, will be.	s.	d.
Of Argand's lamp, with spermaceti oil	0	0¾ per hour.
Mould-candles	0	3½
Wax-candles	1	2

The following Table by Dr. Ure shows the relative intensities of light afforded by the combustion of different candles:—

Number in a Pound.	Duration of a Candle.	Weight in Grains.	Consumption per Hour: Grains.	Proportion of Light.	Economy of Light.	Candles equal to 1 Argand.
10 mould	5h. 9m.	682	132	12¼	68	5·7
10 dip	4 36	672	150	13	65½	5·25
8 mould	6 31	856	132	10½	59½	6·6
6 ditto	7 2½	1160	163	14¾	66	5·
4 ditto	9 36	1787	186	20¼	80	3·5
Argand oil-flame	512	69·4	100	

A pint of the best sperm oil, weighing about 13 ounces, burns, in a well-trimmed Argand, about 10 hours*.

* The following answers to some questions put by the Committee of the Athenæum Club to Mr. Faraday, are so generally applicable, that I venture to introduce them here. "Q. What is the ratio of light of an oil and gas burner?—In an excellent Argand oil lamp, compared with a 15-hole gas burner, the light of the gas was to that of the oil as 21 to 13. Q. What is the ratio of heat?—In experiments made to determine the heat evolved for *equal quantities of light* from oil and gas burning brightly from Argand burners, the heat from the oil being 2, that from the gas was nearly 3. Q. Is either sulphurous or sulphuric acid formed by the combustion of coal-gas in the ordinary way?—A little sulphurous or sulphuric acid is generally formed from the combustion of coal-gas. If well-purified gas be used this product is rarely sensible: it is less sen-

sible as sulphuric than as sulphurous acid. Upon closely questioning persons who have declared they smelt the sulphur from gas, I have usually found they meant something else—generally the oppressive heat, or the dry sensation, or the smell of a little gas unburnt, none of which have anything to do with the sulphur product from gas. Q. From a gas light, properly regulated, does unburned gas escape?—I do not believe that any gas escapes unburnt from a gas light well regulated. It is far more likely that oil vapour should escape unconsumed from an oil burner than gas from a gas burner. Q. Will an oil or gas light soonest soil the ceiling of a room?—Neither oil nor gas ought to soil, or will soil, the ceiling of a room, if well regulated. Either will do so when badly regulated. I think, of the two, oil is most liable to do so; because of

CARBON AND NITROGEN. BICARBURET OF NITROGEN. CYANOGEN. PRUSSINE. ($2\text{car} + n$) or *Cy*, or NC_2 .—This gaseous compound was discovered in 1815, by Gay Lussac (*Ann. de Chim.*, xcv.), and termed *cyanogen* (from *κυανος*, blue, and *γενναω*, I generate), in consequence of its being essential to the formation of *Prussian blue*. It may be obtained from dry and pure crystals of *cyanuret of mercury*. This substance, when heated in a small glass tube to dull redness, becomes black, and a quantity of mercury passes over and condenses in the cold part of the tube: the gas which is at the same time evolved must be collected over mercury. Under a pressure of between three and four atmospheres at the temperature of 45° , Mr. Faraday condensed cyanogen into a limpid colourless liquid, of a specific gravity of about 0.9, and a refractive power rather less than that of water. When a tube containing it was opened, the expansion within appeared inconsiderable, and the liquid slowly evaporated, producing intense cold. It does not conduct electricity.

At common temperatures and pressures, cyanogen is a colourless gas, and has a penetrating and peculiar smell, somewhat resembling that of bitter almonds. When a lighted taper is dipped into it, it is immediately extinguished, but the gas takes fire and burns upon the surface, in

the changes which take place in the wick, in the temperature of the oil, &c., during burning, and which do not occur with a gas lamp properly regulated.

Q. What are the comparative effects of oil and gas lights on the quality of the air, light for light?—It is exceedingly difficult to ascertain, and, if ascertained, to describe correctly the effects of lights on air, so as to convey a just opinion of their influence; thus, their power of heating is of advantage and desirable up to a certain point, and above that point is unpleasant and disagreeable: but that point depends upon many other things as well as the lights, and, what is still more important, differs for different persons, so that it becomes impossible to please all. Gas light will heat air faster than oil light; it therefore at first does good quicker, and afterwards does harm quicker than oil. As to the proportionate deterioration of air by the oxygen abstracted, I think it probable that gas would, *light for light*, have the greatest effect; but I do not believe that effect would be sensible in either case. As to the deterioration of air by the sulphurous acid and unburnt gas thrown into the room, I think little of it. Q. What are the comparative qualities of the light from oil and gas?—When the oil was burning in its best manner, still it gave a much yellower flame than the gas; the whiteness of the gas flame is a necessary consequence of its higher temperature.

Q. Taking all the circumstances into consideration, what, in your opinion, is the cause of the oppressive feeling complained of in certain rooms in the Athenæum?—In my opinion the principal cause of complaint is of the following nature: a house has been built, and every endeavour made to render floors, ceilings, windows, walls, and doors, tight and close; the rooms in it are well warmed during the day, and are brought to such a temperature and state that the first person who enters is fully satisfied; from fifty to two hundred persons are then introduced, evolving both heat and effluvia; a number of powerful gas burners are next put into and continue in action; and when the injurious agency of these causes is continued for one, two, or three hours, complaints are made that the heat is oppressive, or the odour unpleasant. Things are arranged so as to produce a perfect effect under one set of circumstances, and then, changing the circumstances, the effect is expected to remain the same, though it must of necessity be different. The large room and the library are made quite warm enough by daylight, when there are only a few persons there: then they are lighted, many persons enter, and they must of course very soon expect an oppressive sensation. I have no hesitation in believing that the cause of these complaints might be removed by extending and adjusting the system of ventilation."

contact with air, with a beautiful and very characteristic purple flame. Its specific gravity to hydrogen is as 26 to 1; and to common air as 1·82 to 1; 100 cubic inches weigh 55·5 grains, (56·472 grains, TURNER; or at the temperature of 32°, 59·2023 grains, THOMSON.) It sustains a high temperature without decomposition. Water dissolves 4·5 volumes, and alcohol 23 volumes, of this gas. Sulphuric ether and oil of turpentine also absorb it. The aqueous solution reddens vegetable blues; and, according to Vauquelin (*Ann. de Ch. et Ph.*, Oct. 1818), is subject to spontaneous decomposition, being gradually converted into carbonic and hydrocyanic acids, ammonia, a peculiar acid, which he calls the *cyanic*, and a brown substance containing carbon: the ammonia saturates the acids, and the carbonaceous compound is deposited. These changes are referable to the mutual reaction of the elements of cyanogen upon those of water. According to Wöhler (*Ann. de Ch. et Ph.*, lxxiii. 73), the mutual action of cyanogen and water is attended by the production of cyanic acid and ammonia, which, by combination, generate *urea*.

Cyanogen may be analyzed by detonation with oxygen, or by passing it over red-hot oxide of copper. One volume, detonated over mercury, with two of oxygen, produces two volumes of carbonic acid and one of nitrogen: whence it appears that cyanogen consists of its own volume of nitrogen, combined with carbon sufficient to form two volumes of carbonic acid; or of equal volumes of nitrogen and gaseous carbon; and if so constituted, as

	Grains.
100 cubic inches of carbon vapour weigh	25·4
100 " nitrogen gas	30·1
100 " cyanogen vapour should weigh	55·5

Cyanogen, therefore, is constituted of

				Vols.	Sp. Gr.
Carbon	2	12	46·1	1	0·843
Nitrogen	1	14	53·9	1	0·976
Cyanogen	1	26	100·0	1	1·819

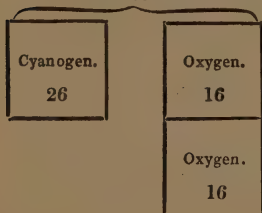
or it may be represented as annexed:

Carbon. 6	Nitrogen.	=	Cyanogen.
6	14		26

and the following diagrams show the result of its detonation with oxygen:

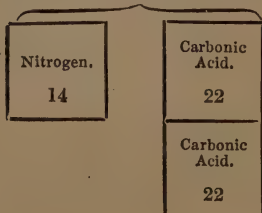
Before detonation.

One volume of Cyanogen and two of Oxygen.



After detonation.

One volume of Nitrogen and two of Carbonic Acid.



Iodine, sulphur, and phosphorus, may be sublimed in cyanogen without change; but when they are heated in contact with cyanuret of mercury, compounds of those bodies with cyanogen are the result. It also combines with the metals, and constitutes compounds which might be called *nitrocarburets*: they are usually called *cyanurets*, or *cyanides*. The cyanurets also combine with each other, and produce an extensive and curious class of salts which have been termed *double cyanurets*. As a salifying body, therefore, cyanogen may be compared to chlorine, iodine, &c., for it not only combines, as a simple body would do, with the metals, but also forms a hydracid with hydrogen; in some of its properties it bears an analogy to sulphur.

CARBURET OF NITROGEN.—I employ this term to designate the brown matter which remains in the retort after the preparation of cyanogen from cyanuret of mercury, and which, according to Mr. Johnston (*BREWSTER'S Journal*, Second Series, i. 75), is a solid compound of carbon and nitrogen, isomeric with cyanogen. The same compound is produced by the action of mercury on a saturated alcoholic solution of cyanogen, and is also probably formed by charring certain animal substances. It is soluble in the alkalis. Heated in the air it yields several definite compounds of carbon and nitrogen in succession, and ultimately leaves a residue containing 1 atom of carbon and 1 of nitrogen, so that the carbon gradually burns away, leaving the nitrogen fixed till a *protocarburet* is formed.

CYANOGEN AND OXYGEN.—According to Liebig and Wöhler, there are three distinct isomeric combinations of cyanogen and oxygen, which may be represented as follows:—

1. Cyanic acid . . . ($cy + o$)
2. Fulminic acid . . . ($2\ cy + 2\ o$)
3. Cyanuric acid . . . ($3\ cy + 3\ o$)

CYANIC ACID. ($2\ car. + n + o$) or ($cy + o$) or cy' .—The existence of an acid composed of cyanogen and oxygen, was first suspected by Vauquelin; but for our knowledge of its composition, and properties, we are indebted to Wöhler and Liebig. When cyanogen is passed into alkaline solutions it is absorbed, and a cyanuret and cyanate are formed, which, however, cannot be effectually separated, so that, in this respect, the action of cyanogen on the alkaline solution corresponds with that of chlorine and of iodine. But, according to Wöhler, a true cyanate of potassa may be obtained by exposing a mixture of black oxide of manganese and ferrocyanuret of potassium to a dull red heat, carefully avoiding too high a temperature, and boiling the resulting compound in spirit of wine of the specific gravity of 0.86. As the solution cools, tabular crystals of *cyanate of potassa* are deposited. (*Ann. de Ch. et Ph.*, xxvii. 196.) When these are dissolved in cold water the solution slowly decomposes, and, if boiled, carbonic acid and ammonia are produced, in consequence of the re-action of the elements present. Cyanic acid forms a soluble salt with baryta, but it occasions insoluble precipitates in solutions of lead, mercury, and silver, and these cyanates may be decomposed by diffusing them through water, and exposing them to the action of a current of sulphuretted hydrogen, not in excess. A sour pungent liquid, smelling like acetic

acid, is thus obtained, but it is very prone to decomposition, and in a few hours becomes converted into carbonate of ammonia. (LIEBIG, *Ann. de Ch. et Ph.*, xxxiii. 208.)

According to the analysis of Wöhler (*Ann. de Ch. et Ph.*, xx. and xxvii.), corroborated by the experiments of Liebig, anhydrous cyanic acid consists of

Carbon	2	12	35.2	Cyanogen	1	26	76.3
Nitrogen	1	14	41.1				
Oxygen	1	8	23.7	Oxygen	1	8	23.7
Cyanic acid	1	34	100.0		1	34	100.0

But the anhydrous acid is only known in combination with bases, or with water, as obtained above, or as afforded by the distillation of dry cyanuric acid; in this state it contains

		Liebig.			
Carbon	} Cyanogen	1	26	60.1	60.23
Nitrogen		1	8	18.6	18.71
Oxygen		1	9	21.3	21.06
Water					
Hydrate of cyanic acid, or }		1	43	100.0	100.00
Cyanate of water					

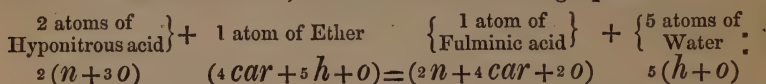
The facility of the conversion of an aqueous solution of cyanic acid into bicarbonate of ammonia, will be apparent on reference to their atomic composition, for 1 equivalent of cyanic acid with 3 of water, or $(2\text{ car} + n + o) + (3h + 3o)$, are equal to 1 equivalent of bicarbonate of ammonia $2(car + 2o) + (n + 3h)$: or, represented in abbreviated symbols, $cy' + 3q = (2car' + A.)$

CYANATE OF AMMONIA. ($A + cy'$).—There are two isomeric cyanates of ammonia. When ammonia and the vapour of hydrated cyanic acid are brought together they combine into a white flocculent and crystallized substance, which, according to Liebig (*Chimie Organique*, i. 126), contains more ammonia than corresponds with a neutral salt: it is, therefore, apparently a basic salt, but in its properties it agrees with the ordinary cyanates; heated with acids it effervesces, and with alkalis it disengages ammonia; but when gently heated, either in the dry state, or in solution, it gives out ammonia and becomes converted into *urea*, which will be described amongst organic products.

CYANATES.—The salts of the cyanic acid are distinguished by the peculiar results of the action of most other acids upon them. If an acid be added to a dry or a dissolved cyanate, effervescence soon ensues, attended by a strong odour of cyanic acid, and if hydrate of lime be then added ammonia is evolved, which it was impossible to detect in the original cyanate. The cyanates of the alkalis are soluble; all the others insoluble. All the soluble cyanates, excepting that of ammonia, are resolved into ammonia and carbonates, when boiled in aqueous solution.

FULMINIC ACID. $(2n + 4car + 2o)$ or $(2cy + 2o)$.—Under the articles *Mercury* and *Silver*, the process for preparing detonating compounds of those metals, by acting upon their nitric solutions by alcohol, is stated:

the experiments of Liebig, and Gay Lussac (*Ann. de Ch. et Ph.*, xxiv. and xxv.), lead to the inference, that in these combinations the metallic oxides are united to an acid containing the same elements, and in the same relative proportions, as the cyanic acid, to which, in that particular state of combination, the term *Fulminic Acid* has been applied; but the equivalent of the fulminic acid is double that of the cyanic, or = 68. According to Liebig, the results of the action of nitric acid upon alcohol, are hyponitrous acid on the one hand, and on the other, aldehyd, and formic, and oxalic acids. In the presence of oxide of mercury or oxide of silver, 2 atoms of hyponitrous acid and 1 atom of ether (the elements of which are contained in the alcohol) become converted into fulminic acid, which unites to the metallic oxide, as shown in the following equation:—



When the vapour of nitrous acid is passed into a saturated solution of nitrate of silver in alcohol, there is an immediate precipitation of fulminate of silver.

Fulminic acid has not been isolated from the bases with which it is combined; at the moment of its separation by a stronger acid it is resolved into hydrocyanic acid and other products.

If regarded as anhydrous, it consists of

Cyanogen	2	52	76.5	Liebig.
Oxygen	2	16	23.5	76.74
				23.26
Fulminic acid	1	68	100.0	100.00

FULMINATES.—Liebig represents these salts as containing either 2 atoms of fixed base (neutral fulminates) or 1 atom of fixed base and 1 atom of water; the latter have an acid reaction. The 2 atoms of fixed base may be represented by 2 atoms of the oxide of an easily reducible metal, or by 2 atoms of the oxides of two different metals, also easily reducible. Thus for example, 2 atoms of oxide of copper, 2 atoms of oxide of silver, 2 atoms of oxide of mercury, or 1 atom of oxide of copper and 1 atom of oxide of silver, may combine with 1 atom of fulminic acid, to form a neutral salt. The fulminates with an alkaline base include 1 atom of alkaline oxide and 1 atom of easily reducible oxide, as, for example, 1 atom of oxide of silver and 1 atom of potassa, baryta, strontia, or oxide of zinc. There are no fulminates of two alkaline bases. When a fulminate of the first class, containing 2 atoms of oxide of silver or of oxide of mercury, is treated by an alkali, only half the oxide is replaced by 1 atom of the alkali. This singular property seems to indicate an intimate relation between the oxygen of the acids and of the oxides with which they combine. (*Chimie Organique.*)

CYANURIC ACID. ($3Cy+3O$).—These elements are only known in combination with 3 atoms of water, or as ($3Cy+3O+3Q$). Scheele first described this acid under the name of *pyrouric acid*; Serullas afterwards obtained it by another process, and termed it *cyanic acid*. (*Ann. de Ch. et Ph.*, xxxviii.) Its real nature and properties were first ascertained by Liebig and Wöhler. When urea is heated beyond its fusing point, it

evolves ammonia and is converted into a gray substance: if this be dissolved in sulphuric acid, and nitric acid dropped in till the solution becomes colourless, and then added to an equal volume of water, crystals of pure cyanuric acid are deposited. Liebig obtained cyanuric acid from a substance which is produced by the decomposition of the sulphocyanuret of ammonium, and which he calls *Melam*. Dry melam is dissolved by a gentle heat in strong sulphuric acid, and then added to 20 parts of water: the mixture is kept near its boiling-point for several days, till it no longer gives a white precipitate with ammonia; it is then evaporated and crystallized. These crystals, which are rhombic prisms, are composed of 1 atom of the terhydrated cyanuric acid and 4 atoms of water; these they lose by exposure to air, and fall into a white powder, sparingly soluble in water, inodorous, and slightly reddening litmus. It dissolves without decomposition in the strong acids, but by long boiling is converted into carbonic acid and ammonia. The prismatic crystals of cyanuric acid, dried at a temperature of 212° , lose 4 atoms of water of crystallization, and retain 3 atoms of combined water; in this latter state of composition the acid may be obtained in flattened octoëdra, or oblique quadrilateral prisms, terminated by diëdral summits, by cooling its boiling saturated solution in nitric or hydrochloric acid. The following, therefore, is the composition of the anhydrous cyanuric acid, as it exists in combination with bases, and which cannot be isolated:—

Cyanogen	3	78	76·5
Oxygen	3	24	23·5
<hr/>			
Anhydrous cyanuric acid	1	102	100·0

The crystallized hydrate (cyanurate of water) consists of

Anhydrous acid . . .	1	102	79
Water (combined) . . .	3	27	21
<hr/>			
Hydrate of cyanuric acid	1	129	100

And the prismatic crystals contain

Hydrate of cyanuric acid	1	129	78·2
Water of crystallization	4	36	21·8
<hr/>			
Crystals of cyanuric acid	1	165	100·0

CYANURATE OF AMMONIA.—This salt crystallizes in shining white prisms, efflorescent, and losing ammonia when heated; dried in vacuo it contains the elements of 1 atom of anhydrous cyanuric acid, 1 atom of ammonia, and four atoms of water.

CYANURATES.—The cyanuric acid combines with 3 atoms of bases, which are represented by the 3 atoms of water in the hydrate of the cyanuric acid. This water is either wholly or partially replaced by metallic oxides. The alkaline oxides form two series of cyanurates; in the one, the salt contains 1 atom of anhydrous acid, 1 atom of basic oxide, and 2 atoms of basic water; in the other, 1 atom of acid, 2 atoms of oxide, and 1 of water (as in the corresponding phosphates). There are no salts constituted of 1 atom of acid with 3 of alkaline oxide. But the cyanurate of silver is anhydrous, and contains 3 atoms of oxide

of silver; so that the relative proportion of elements *per cent.* is the same in the *cyanate*, the *fulminate*, and the *cyanurate of silver*, but they differ in the mode of their constitution. All the cyanurates are decomposed by nitric and by hydrochloric acid. The cyanuric acid which crystallizes from a solution of a cyanurate so decomposed, contains no trace of the oxide with which it was combined. The salts with alkaline bases fuse when heated, and leave an alkaline cyanate, whilst cyanate of ammonia, hydrated cyanic acid, carbonic acid, and nitrogen, are evolved. (LIEBIG, *Chimie Organique*.)

CYAMELIDE. INSOLUBLE CYANURIC ACID.—The hydrate of cyanuric acid, when kept for some time, becomes hard and white (like porcelain). In this state it is insoluble in water, dilute acids, alcohol, and ether; it is dissolved and decomposed by caustic alkalis, into ammonia, and alkaline cyanates and cyanurates.

CYANOGEN AND CHLORINE. CYANURET OF CHLORINE. CHLOROCYANIC ACID. (*cy* + *c*).—Gay Lussac procured this compound by passing a current of chlorine through a solution of hydrocyanic acid in water, till the liquid discoloured a dilute solution of indigo in sulphuric acid. He then deprived it of excess of chlorine by agitation with mercury, and submitted it to careful distillation, by which an elastic fluid was evolved, consisting of a mixture of carbonic and chlorocyanic acids; and which, when condensed into water, furnishes a strong-smelling colourless solution, which reddens litmus. According to the statement of Liebig, when excess of chlorine is passed into the aqueous solution of hydrocyanic acid, chloride of cyanogen, hydrochloric acid, and free chlorine, are contained in the liquid. When gently heated the chloride of cyanogen is disengaged, and is obtained pure by passing it through a tube containing chloride of calcium. It is gaseous at common temperatures, has an insupportable and pungent odour, and when cooled to 0° crystallizes in long needles which fuse at 5° and boil at 10° , but under a pressure of about 4 atmospheres remain liquid at 70° . When kept in this state in tubes hermetically sealed it forms, according to Persoz, white crystals of a solid chloride of cyanogen, having the same composition as the following. Water dissolves 25, ether 50, and alcohol 100 volumes of the gas. It is decomposed by the alkalis. When moist cyanuret of mercury is exposed in chlorine to the action of solar rays, a heavy yellow liquid is formed, insoluble in water, and having the odour of chloride of cyanogen; the same substance appears to be formed by the action of chlorine on fulminate of silver.

It appears from the researches of Gay Lussac and Serullas (*Ann. de Ch. et Ph.*, xcv. 205), that 100 volumes of the gaseous cyanuret of chlorine consist of 50 volumes of cyanogen + 50 volumes of chlorine, the gases combining without a change of volume: accordingly, as

		Grains.
50	cubic inches of cyanogen weigh	27.7
50	" chlorine	38.0
100	" cyanuret of chlorine should weigh	65.7

and it is a compound of

							Vols.	Sp. Gr.
Carbon . . .	2 . . .	12 . . .	19.4	} Cyanogen 1 . . .	26 . . .	42 . . .	0.5 . . .	0.91
Nitrogen . .	1 . . .	14 . . .	22.6					
Chlorine . .	1 . . .	36 . . .	58.0		1 . . .	36 . . .	58 . . .	0.5 . . . 1.23
<hr/>					<hr/>	<hr/>	<hr/>	<hr/>
Chlorocyanic vapour 1	62	100.0			1	62	100	1. 2.14

SOLID CHLORIDE OF CYANOGEN.—When a mixture of dry chlorine and hydrocyanic acid is exposed to the sun's rays, hydrochloric acid and solid chloride of cyanogen are formed: the latter, when pure, is white and sublimates in acicular crystals; it has a penetrating odour resembling that of the excrement of mice; its taste is pungent; its specific gravity 1.32; it fuses at 284° , and sublimates at 374° . When digested in hot water, it is resolved into cyanuric and hydrochloric acids. It is soluble without decomposition in alcohol and ether. According to Bineau 1 volume of the vapour of this compound is constituted of 1.5 of chlorine, and 1.5 cyanogen, so that the 3 volumes are condensed into 1. It combines with ammonia. According to Liebig, this chloride corresponds to cyanuric acid, and is represented by the formula ($3C + 3Cy$).

CHLOROCYANATE OF AMMONIA.—One volume of chlorocyanic vapour and two volumes of ammonia condense with slight evolution of heat into white granular crystals, permanent in the air, and inodorous. This salt fuses when heated, and yields ammonia and hydrochlorate of ammonia, leaving a yellow residue, having the characters of *mellon*. (BINEAU, *Ann. de Ch. et Ph.*, LXVII. 237, and LXX. 255.)

CYANOGEN AND IODINE. CYANURET OF IODINE. ($Cy + i$).—This compound was first obtained by Davy (*Quarterly Journal*, i. 289), and afterwards more fully examined by Serullas. (*Ann. de Ch. et Ph.*, xxvii.) It may be obtained by heating in a platinum capsule a mixture of one part of iodine with two of pulverized bicyanuret of mercury; they soon react upon each other, and as soon as white fumes arise the capsule may be placed under a dry bell glass; the action goes on and a white flocculent product is formed. Mitscherlich obtains this compound by distilling the mixture of iodine and cyanuret of mercury with a little water, in a retort; it yields acicular crystals of an acrid taste, pungent odour, and exciting a flow of tears. It is very poisonous. It is heavier than sulphuric acid. It dissolves in water, and still more readily in alcohol, and the solutions do not redden litmus: alkaline solutions decompose it, forming iodates and hydrocyanates. It is instantly decomposed by solution of sulphurous acid; iodine is disengaged, and hydrocyanic evolved. Dry sulphurous acid gas does not act upon it. From the experiments of Serullas, it is probably composed of

Carbon	2 . . .	12 . . .	3.0	} Cyanogen 1 . . .	26 . . .	17.3
Nitrogen	1 . . .	14 . . .	9.3			
Iodine	1 . . .	126 . . .	82.7		1 . . .	126 . . . 82.7
	<hr/>	<hr/>	<hr/>		<hr/>	<hr/>
	1	152	100.0		1	152 100.0

According to Bineau the cyanuret of iodine forms a definite liquid compound with ammonia. (*Ann. de Ch. et Ph.*, LXVII. 235.)

CYANOGEN AND BROMINE. CYANURET OF BROMINE. ($cy + b$).—Two parts of dry bicianuret of mercury are put into a small tubulated retort, or into the bottom of a sealed tube plunged into a freezing mixture: one part of bromine is then added; a vivid action ensues, and so much heat is evolved, that if the temperature were not kept down the bromine would be volatilized; bromide of mercury and cyanuret of bromine are formed; the latter crystallizes in needles in the upper part of the tube, whence it may be sublimed into a cold receiver by the application of a gentle heat: sometimes it forms small cubic crystals. In many respects its physical properties resemble those of cyanuret of iodine; its odour is excessively pungent, and it is so volatile as to exist in vapour at temperatures above 60° . It is more soluble in water and alcohol than the compound of iodine. Solution of potassa transforms it into cyanate and bromide of potassium. The solution furnishes a precipitate when added to nitrate of silver, composed of cyanuret and bromide of silver, easily separable by ammonia, which dissolves the latter but not the former. Like the cyanuret of iodine, it is extremely deleterious to animals. One grain of it dissolved in a little water, and introduced into the œsophagus of a rabbit, occasioned instant death, as rapidly as hydrocyanic acid; it cannot, therefore, be examined without risk. Its composition has not been accurately determined. (SERULLAS, *Ann. de Ch. et Ph.*, vol. xxxiv. p. 100.) It combines with ammonia in two proportions, forming a solid and liquid compound. (BINEAU, *Ann. de Ch. et Ph.*, lxx. 257.)

CYANOGEN AND HYDROGEN. HYDROCYANIC ACID. CYANHYDRIC ACID. PRUSSIC ACID. ($cy + h$) or hcy or CyH .—This compound was first obtained by Scheele (*Stockholm Trans.*, 1782, 1783), and its composition ascertained by Berthollet in 1787, and by Clouet (*Ann. de Ch. et Ph.*, xi. 30). It was not, however, till the discovery of cyanogen by Gay Lussac, in 1815, that its real nature was understood, and its components accurately determined. Cyanogen and hydrogen have no tendency to direct combination, but by the action of certain acids on the metallic cyanurets, hydrocyanic acid is formed by double decomposition: in this way it is obtained by the action of hydrochloric acid on bicianuret of mercury, and the process is conducted as follows:—Introduce the cyanuret into a tubulated glass retort, and pour upon it rather less than its weight of hydrochloric acid (sp. gr. 1.20). Adapt a horizontal tube to the beak of the retort, about two feet long and half an inch diameter; fill the first third of the tube next the retort with small pieces of white marble, and the other two-thirds with fragments of fused chloride of calcium; adapt to its extremity a small receiver, surrounded by a freezing mixture; on applying a gentle heat to the retort, hydrocyanic vapour will pass through the tube, and become condensed in the cold receiver; any portion of hydrochloric acid and watery vapour that may arise along with it will be detained by the carbonate and chloride; after this part of the process the whole length of the tube should be gently heated, to expel the residuary hydrocyanic acid. As the extrication of carbonic acid from the marble is not only inconvenient, but liable to carry off hydrocyanic acid, the distillation of any portion of hydrochloric acid should, as far as possible, be prevented, by placing the retort in a horizontal position, using

the least possible quantity of it, and employing not more than a sufficient heat.

Another mode of obtaining hydrocyanic acid consists in placing cyanuret of mercury in a tube connected with a cooled receiver: sulphuretted hydrogen is then passed over the cyanuret, the sulphur of which combines with the mercury to form a sulphuret of mercury, and the hydrogen unites to the cyanogen to form hydrocyanic acid; the whole of which may be easily driven, by the application of a gentle heat, into the cold receiver, and there condensed. (VAUQUELIN.)

A third process for the production of anhydrous hydrocyanic acid is to distil by a gentle heat 15 parts of finely powdered ferrocyanuret of potassium, with a mixture of 9 parts of sulphuric acid and 9 of water: the product must be collected in a well-cooled receiver containing 5 parts of broken chloride of calcium: the distillation is stopped as soon as the chloride of calcium is covered by the liquid hydrocyanic acid, which is then carefully poured off and preserved in a well-stopped phial. (TRAUTWEIN.)

The hydrocyanic acid thus obtained is a limpid liquid of a strong pungent odour, very like that of bitter almonds, in which, and in other species of *amygdalus* and *prunus*, we shall afterwards recognise it. Its taste is acrid, and it is highly poisonous, so that the utmost care should be taken to avoid the inhalation of its vapour. It volatilizes so rapidly as to freeze itself, when a drop of it is placed upon a glass plate. Its specific gravity at 45° is 0.705, and at 64° 0.696; and the specific gravity of its vapour, as experimentally determined by Gay Lussac, is 0.9476: it boils at 80° , and congeals at 3 or 4° above 0° in its ordinary state, but when it is perfectly anhydrous it remains liquid according to Schultz at -40° . It burns with a bright flame. It scarcely affects the blue of litmus. It is liable to spontaneous decomposition, especially under the influence of light, becoming brown and evolving ammonia, changes which are prevented by the presence of minute portions of other acids. When water is present, the concentrated inorganic acids resolve it into ammonia and formic acid: 3 atoms of water and 2 of hydrocyanic acid, include the elements of 1 atom of formic acid and 1 of ammonia. It is resolved by chlorine into hydrochloric acid and chloride of cyanogen. The easily reducible oxides (of mercury and silver) decompose hydrocyanic acid, and yield water and a metallic cyanuret. When lime or baryta are heated to redness in hydrocyanic vapour, they afford cyanurets and cyanates, and hydrogen is evolved.

In the voltaic circuit hydrocyanic acid yields hydrogen at the negative, and cyanogen at the positive, electrode. When its vapour is mixed with oxygen, it may be burned by the electric spark, in which case two volumes of hydrocyanic vapour require for perfect combustion two volumes and a half of oxygen: the results are water, two volumes of carbonic acid, and one volume of nitrogen. When potassium is heated in the gas, cyanuret of potassium is formed, and hydrogen, equal to half the volume of the acid, liberated: it appears, therefore, that there is the strictest analogy between the hydrocyanic and the other hydracids, and that one volume of cyanogen and one of hydrogen form two volumes of the vapour hydrocyanic acid: and as

50 cubic inches of cyanogen weigh	Grains. 27·74
50 " hydrogen	1·06
<hr/>	
100 " hydrocyanic acid should weigh .	28·80

Hydrocyanic acid, therefore, is a compound of

						Vols.	Sp. Gr.
Carbon 2 . 12] . 44·5	} Cyanogen	1 . 26 . 96·3	0·5 . 0·91				
Nitrogen 1 . 14 . 51·8							
Hydrogen 1 . 1 . 3·7		Hydrogen 1 . 1 . 3·7	0·5 . 0·03				
<hr/>							
Hydrocyanic acid 1 . 27 . 100·0		1 . 27 . 100	1 . 0·94				

Hydrocyanic acid is used in medicine as a sedative, and several formulæ have been given for its preparation, so as at once to obtain it of a convenient strength for pharmaceutical purposes. The Pharmacopœia directs the decomposition of ferrocyanuret of potassium by dilute sulphuric acid, and the state of dilution of this hydrocyanic acid is such that it contains 2 per cent. of the real acid. (See *Ferrocyanuret of Potassium* and *Cyanuret of Silver*.)

The specific gravity of hydrocyanic acid when thus largely diluted cannot be resorted to as a criterion of its strength, hence other modes of determining this have been adopted. Dr. Ure recommends the following:—To 100 grains, or any other convenient quantity of the acid, contained in a small phial, add, in succession, small quantities of pure peroxide of mercury in very fine powder, till it ceases to be dissolved on agitation: the weight of the oxide taken up, being divided by 4, gives a quotient representing the quantity of real acid present. By weighing out beforehand, on a watch-glass, 40 or 50 grains of the peroxide, the residual weight of it shows at once the quantity expended. (*Quarterly Journal*, xiii. 312.) Dr. Ure's *Essay* also contains a table of the specific gravity of the acid of various degrees of dilution, and directions for detecting the presence of hydrochloric acid in it. The strength of the pharmaceutical hydrocyanic acid may also be determined by the weight of the precipitate obtained by nitrate of silver, (cyanuret of silver,) every 3 grains of which when well washed and dried, are equivalent to 1 grain of anhydrous hydrocyanic acid.

Another mode of obtaining dilute hydrocyanic acid is to pass sulphuretted hydrogen through water, holding in solution a known quantity of bicyanuret of mercury, so as completely to decompose it: the excess of sulphuretted hydrogen is then abstracted by carbonate of lead, and the solution of hydrocyanic acid filtered: but in this process it is difficult to obtain a perfectly clear and colourless solution without the addition of a drop or two of hydrochloric, or sulphuric acid.

A third process is that suggested by Mr. Clarke, of Glasgow. (THOMSON'S *System*, ii. 220.) In 100 drachms of water dissolve eight drachms and a quarter of *cyanuret of potassium*, and add to the solution eighteen drachms and a half of crystallized tartaric acid, previously dissolved in twenty drachms of water. A double decomposition takes place; bitartrate of potassa falls down, and about 120 drachms of water remain, holding in solution $3\frac{3}{8}$ drachms of hydrocyanic acid; or 2·81 per cent. of the solution is hydrocyanic acid. A little bitartrate of potassa

also remains, which may be avoided by using a little alcohol mixed with the water.

A fourth process recommended by Giese, (*TURNER'S Elements*.) is as follows: 20 drachms of ferrocyanuret of potassium are dissolved in 80 of water, and with the solution is mixed a dilute acid made previously with 18 drachms by weight of strong sulphuric acid, and 40 drachms of water, and allowed to cool. The dilute hydrocyanic acid is then distilled off, and if the amount is not 120 drachms, distilled water is added to make up that weight. This is nearly the process of our Pharmacopœia.

As hydrocyanic acid in its dilute state is liable to decomposition, it should be prepared in small quantities and preserved in well-stopped phials out of the presence of light: or a very minute addition of dilute sulphuric acid may be made to it, by which its tendency to change is prevented.

When dilute hydrocyanic is pure, it leaves no residue on evaporation: hydrochloric acid is detected in it by heating it in a water-bath so as to expel the hydrocyanic acid, and then testing by sulphate of silver: if sulphuric acid be present, it occasions a precipitate on adding nitrate of baryta, which is insoluble in nitric acid.

The virulently poisonous nature of this acid has led to its occasional administration with criminal intentions: the mode in which it produces death, and the symptoms, are enumerated by medical and physiological writers, but the chemist may be called upon to suggest means of detecting it: this is generally easily effected in consequence of its very peculiar odour; and if the fluid containing it be agitated with finely-powdered peroxide of mercury, crystals of cyanuret of mercury may be obtained on evaporation. The following is an accurate test of its presence, originally suggested by Scheele: to the suspected liquid add a solution of *protosulphate* of iron, and afterwards drop in pure potassa in slight excess, and after a short exposure to the air, redissolve the precipitate in hydrochloric acid. If hydrocyanic acid be present, the tint of Prussian blue will appear. Except in cases of recent examination it is not easily detected in the contents of the stomach after death, since it is decomposed with their putrefaction. In such cases Leuret and Lassaigne have recommended the following procedure: The stomach and its contents, cut into pieces, are carefully distilled with water slightly acidulated by sulphuric acid: the volatile products are condensed in a receiver surrounded by ice, and examined by the above-mentioned method: in such cases the acid is also generally recognised by its odour.

Ammonia, and chlorine, are the most effective antidotes in cases of poisoning by hydrocyanic acid; but for its toxicological history I must refer to writers on that subject. (*CHRISTISON, On Poisons. PEREIRA, Elem. of Mat. Med.*)

HYDROCYANATE OF AMMONIA. CYANURET OF AMMONIUM.—This salt may be obtained by mixing hydrocyanic acid with liquid ammonia; it is anhydrous, and crystallizes in cubes or small prisms, and is extremely volatile. Bineau obtained it by heating equivalents of cyanuret of mercury, or of dried ferrocyanuret of potassium, with hydrochlorate of ammonia. (*Ann. de Ch. et Ph.*, Lxvii. 231.) Dr. Thomson states, that

when Prussian blue is exposed to a red heat, and the products of its decomposition received over mercury, the glass receiver becomes coated with crystals of this salt. Hydrocyanate of ammonia soon suffers spontaneous change, and it is decomposed by carbonic and other feeble acids. From Bineau's experiments it appears to consist of 17 ammonia + 27 hydrocyanic acid, elements which upon the ammonium theory are equivalent to $(n + 4h) + cy$.

CYANOGEN AND SULPHUR. SULPHOCYANOGEN. CYANURET OF SULPHUR. $(cy + 2s)$.—Sir H. Davy obtained this compound in 1816, by heating a mixture of sulphur and bichcyanuret of mercury. (*Quart. Jour.*, i. 289.) Liebig obtains it by saturating a concentrated solution of sulphocyanuret of potassium with chlorine, or by boiling a soluble metallic sulphocyanuret in dilute nitric acid; it falls in the form of a yellow precipitate, which preserves its colour when dry, and is insoluble in water, alcohol, and ether, but soluble in hot sulphuric acid, from which it is again thrown down by water. It is decomposed by concentrated nitric acid: when heated with potassium, sulphuret, cyanuret, and sulphocyanuret of potassium are formed: subjected to dry distillation, it yields carburet of sulphur, and ultimately nitrogen and cyanogen. (LIEBIG.) By digesting cyanuret of mercury in chloride of sulphur, Lassaigne obtained a compound in brilliant crystals, which he regarded as containing 4 atoms of cyanogen and 1 of sulphur (*Ann. de Ch. et Ph.*, xxxix.), but which, according to Liebig, are a compound of chloride of cyanogen with chloride of sulphur.

The elements of sulphocyanogen are

Carbon	. . . 2	. . . 12	. . . 20·7	} Cyanogen	1	. . . 26	. . . 44·8	
Nitrogen	. . . 1	. . . 14	. . . 24·1					
Sulphur	. . . 2	. . . 32	. . . 55·2		Sulphur	2	. . . 32	. . . 55·2
<hr/>						<hr/>	<hr/>	
Sulphocyanogen	1	58	100·0		1	58	100·0	

CYANOGEN, SULPHUR, AND HYDROGEN.—By mixing cyanogen and sulphuretted hydrogen, Gay Lussac obtained a yellow crystallized compound. (*Ann. de Ch. et Ph.*, xcv.) This probably consists of one atom of cyanogen, and one of sulphuretted hydrogen, and is identical with the compound obtained by passing sulphuretted hydrogen into a saturated alcoholic solution of cyanogen. The mutual action, however, of cyanogen and sulphuretted hydrogen requires to be more minutely examined. We are indebted to Mr. Porrett (*Phil. Trans.*, 1814), for our knowledge of a triple compound of cyanogen, sulphur, and hydrogen, which he termed *sulphuretted chyazic acid*, but the term *sulphocyanic acid*, or *hydrosulphocyanic acid*, is now generally applied to it.

SULPHOCYANIC ACID. HYDROSULPHOCYANIC ACID. SULFOCYANHYDRIC ACID. $(cy + 2s + h)$.—This acid is obtained by decomposing basic sulphocyanuret of lead by dilute sulphuric acid, taking care to leave excess of lead, which is afterwards removed by sulphuretted hydrogen. It is also formed when sulphocyanuret of silver diffused through water is decomposed by sulphuretted hydrogen.

Hydrosulphocyanic acid is colourless, easily decomposed by exposure to

air or heat, yielding among other products a peculiar yellow insoluble powder: chlorine and nitric acid abstract its hydrogen, and evolve sulfo-cyanogen; by their prolonged action cyanic and sulphuric acids are formed, and ultimately ammonia. It reddens the solutions of persalts of iron; it is not poisonous; it exists in the seeds of the cruciferous plants, and in human saliva, and that of the sheep. From the experiments of Porrett (*Ann. of Phil.*, xiii.), confirmed by Berzelius, it consists of

Berzelius.									
Carbon	. . 2	. 12	. 20.3	. 20.30	} Sulphocyanogen	1	. 58	. 98.32	
Nitrogen	. . 1	. 14	. 23.7	. 23.85					
Sulphur	. . 2	. 32	. 54.2	. 54.17					
Hydrogen	. . 1	. 1	. 1.8	. 1.68		Hydrogen	. . 1	. 1	. 1.68
<hr/>									
Hydrosulpho- cyanic acid	} 1	59	100.	100.00					
						1	59	100.00	

SULPHOCYANURET OF AMMONIUM. HYDROSULPHOCYANATE OF AMMONIA. ($cy + 2s$) + ($n + 4h$) or ($cy + h + 2s$) + ($n + 3h$), obtained by saturating ammonia with hydrosulphocyanic acid, and evaporating in vacuo. It is also formed by the mutual action of sulphuret of carbon and alcohol saturated with ammonia. It is decomposed by heat.

CYANURET OF SELENIUM.—No binary compound of cyanogen and selenium has been obtained; but by fusing selenium with ferrocyanuret of potassium, a compound is formed analogous to that of sulphur: the *hydroseleniocyanic acid* has, however, not been separated, so that its existence is as yet hypothetical.

CARBON AND SULPHUR. BISULPHURET OF CARBON. ($car + 2s$) or CS_2 .—This compound was first obtained in 1796 by Lampadius, while distilling a mixture of pyrites and charcoal, and he termed it *alcohol of sulphur*. It was long regarded as a triple compound of carbon, sulphur, and hydrogen, till Clement and Desormes (*Ann. de Chim.*, xlii.), and Cluzel (*Ann. de Chim.*, lxxxiv.), showed the absence of hydrogen; its properties and composition were afterwards more accurately determined by Marcet and Berzelius (*Phil. Trans.*, 1813, p. 171). It is obtained by passing the vapour of sulphur over red-hot charcoal in a porcelain tube; or by distilling about six parts of yellow iron pyrites (bisulphuret of iron) with one of charcoal. The product should be conveyed by a glass tube into cold water. When purified by redistillation, at a low temperature, with chloride of calcium, it is transparent, colourless, and insoluble in water, but soluble in alcohol and ether; its refractive power in regard to light is very considerable. Its specific gravity is 1.272. It boils at 106° , and does not freeze at -60° . It is very volatile and inflammable, and has a pungent taste and peculiar fetid odour. The cold which it produces during evaporation is so intense, that by exposing a thermometer-bulb, covered with fine lint, and moistened with it, in the receiver of an air-pump, the temperature sunk, after exhaustion, to -80° . When a mercurial thermometer was used, the metal froze. Bisulphuret of carbon is soluble in fixed and volatile oils, and it dissolves camphor. It is decomposed, when water is present, by chlorine and iodine; and when potassium is heated in its vapour it burns and decomposes it. It

dissolves sulphur and phosphorus, and the solution often deposits those substances in beautiful crystals. Passed over heated lime or baryta, it produces ignition, and carbonates of those bases, together with sulphurets of calcium and of barium. It is also decomposed by copper and iron at a red heat. Nitrohydrochloric acid converts it into a crystalline compound hydrochloric, sulphurous, and carbonic acids. (BERZELIUS.)

A portion of this compound appears to be frequently formed during the production of inflammable gas from coal, and to be retained in the state of vapour by the gas after its purification by lime; such gas gives a sulphurous smell when burned, although perfectly cleansed from sulphuretted hydrogen, so as not to discolour carbonate of lead. (*Phil. Trans.*, 1820, p. 19.) When its vapour is burned with oxygen it forms carbonic and sulphurous acid. It consists of

		Berthollet, Thenard, Berzelius and Vauquelin.		Berzelius and Marcet.
Carbon	1	15.79	14	15.17
Sulphur	2	84.21	86	84.83
<hr/> Bisulphuret of carbon 1		<hr/> 38	<hr/> 100	<hr/> 100.00

According to Mitscherlich, (who has described a good form of apparatus for obtaining sulphuret of carbon upon a large scale, *Lehrbuch*, i. 153,) the specific gravity of the vapour of this compound is 2.670, and one volume of it is composed of one-third of a volume of sulphur vapour = $\frac{6.654}{3} = 2.218$, and half a volume of carbon vapour = $\frac{0.8438}{2} = 0.4219$.

CARBOSULPHURIC ACID. HYDROXANTHIC ACID.—According to Zeise, carbon and sulphur form a base acidifiable by hydrogen, which he has called *Xanthogene*, from the yellow colour of its compounds: the acid he terms *hydroxanthic acid*. When an alcoholic solution of pure potassa is mixed with bisulphuret of carbon, a compound is obtained, which, evaporated under the exhausted receiver of the air-pump over a surface of sulphuric acid, or exposed to a temperature of 32°, deposits acicular crystals, which become yellow by exposure to air, are very soluble, and from which, upon the addition of dilute hydrochloric or sulphuric acid, an oily-looking fluid, heavier than water, is separated, which is the *hydroxanthic acid*. Exposed to air it becomes covered with an opaque crust: it reddens litmus; tastes sour, astringent, and bitter; is inflammable; and at 212° is decomposed into bisulphuret of carbon and an inflammable gas. The action of ammonia on the sulphuret of carbon is very peculiar, and several new compounds result; but upon these subjects the reader must consult the original sources of information, which scarcely admit of abridgment, and are not very perspicuous in their details. (*Ann. de Ch. et Ph.*, xxi. and xxvi.; *Annals of Phil.*, N. S., iv.; *Quart. Journal*, xviii.)

According to Berzelius, the bisulphuret of carbon is a *sulphur acid*, and in combination with certain metallic sulphurets, or *sulphur bases*, forms a distinct class of *sulphur salts*. (See in reference to these compounds, COUERBE, *Ann. de Ch. et Ph.*, lxi. 25.)

CARBON AND PHOSPHORUS. PHOSPHURET OF CARBON.—To obtain this

compound, Dr. Thomson directs the following process (*System*, ii. 259):—Allow common phosphuret of lime to remain in water till it no longer evolves gas: then add to the liquid excess of hydrochloric acid, agitate for a few moments, and throw the whole upon a filter; phosphuret of carbon remains, which is to be washed and dried. This compound is a soft powder, of a yellowish colour, without taste or smell: exposed to air, it slowly imbibes moisture, and acquires an acid flavour. Exposed to a red heat, it burns, and gradually gives out its phosphorus, the charcoal being prevented burning by a coating of phosphoric acid. It consists of phosphorus 0.62 + carbon 0.38. (THOMSON'S *Annals*, viii. 157.) It would appear from the mode of obtaining this phosphuret, that it forms an ingredient in phosphuret of lime, as usually prepared; it also is obtained in the process for procuring phosphorus, and exists in the red matter which contaminates phosphorus when first distilled.

CARBON AND SELENIUM. CARBURET OF SELENIUM. SELENIURET OF CARBON.—Berzelius has announced the existence of this compound, but has not described its properties. (*Lehrbuch der Chemie*, Dresden, 1826.)

APPENDIX TO THE COMBINATIONS OF CARBON.

PRODUCTS OF THE DECOMPOSITION OF SULPHOCYANOGEN.—Under this head I shall notice several compounds which have been fully described by Liebig (*Chimie Organique*), but the theory and nomenclature of which will probably require future modifications.

MELLON.—When sulphocyanogen is heated to dull redness in a retort, it is resolved into sulphur, sulphuret of carbon, and a peculiar compound of carbon and nitrogen, to which, from its yellow colour, the above name has been given by its discoverer; it consists of 6 atoms of carbon and 4 of nitrogen, and if it be assumed that 4 atoms of sulphocyanogen $4(2\text{CAR} + n + 2\text{S})$ are decomposed, the result will be

4 atoms of sulphur	(4S)
2 „ bisulphuret of carbon	2(CAR + 2S)
1 „ mellon	(6CAR + 4n)

Mellon is a lemon yellow powder insoluble in water and in alcohol, and in dilute sulphuric and hydrochloric acids; it is dissolved, but decomposed by nitric acid and by the fixed alkalis. At a bright red or white heat, it is resolved into 3 volumes of cyanogen and 1 of nitrogen. It combines directly with potassium; light is evolved, and a *mellonuret of potassium* formed. With hydrogen it forms hydromellonic acid. When fused with iodide, bromide, and sulphocyanuret of potassium, it expels iodine, bromine, and sulphocyanogen, and produces mellonuret of potassium.

HYDROMELLONIC ACID ($6\text{CAR} + 4n + h$) is prepared by dissolving mellonuret of potassium in boiling water, and adding nitric, hydrochloric, or sulphuric acid; a white gelatinous precipitate is thrown down, which when dry is yellow, and is a hydrate of hydromellonic acid: it has a slightly acid reaction, and is not decomposed by hydrochloric or nitric acid.

CYANILIC ACID.—Mellon is decomposed by the continued action of boiling nitric acid; the action is attended by the disengagement of gas, and the solution deposits on evaporation colourless and anhydrous octoëdral crystals. On dissolving these crystals in boiling water, the solution yields pearly flakes on cooling, which retain a certain quantity of water. The acid is similar in composition to the cyanuric acid, with which it may be said to be isomeric; its formula according to Liebig being (when anhydrous) ($6\text{ cy} + 6\text{ o}$).

HYDROPER-SULPHOCYANIC ACID. ($\text{cy} + 3\text{ s} + \text{h}$.)—This compound is described by Liebig, (on the authority of Woskresensky,) as obtained by fusing sulphocyanuret of potassium in a stream of dry hydrochloric acid gas; hydrosulphocyanic acid is liberated and immediately decomposed into sulphuret of carbon, hydrocyanic acid, and a yellow product insoluble in water. If this operation be conducted in a retort, a quantity of the yellow product lines the neck of it; it is soluble in boiling alcohol, and precipitates on cooling in the form of a pale yellow crystalline powder sparingly soluble in water: it dissolves in the alkalis, and forms peculiar combinations with the other metallic oxides which are in general insoluble.

MELAM. ($13\text{ car} + 11\text{ n} + 9\text{ h}$.)—When sulphocyanuret of ammonium, or a mixture of 2 parts of sal-ammoniac and 1 of sulphocyanuret of potassium, are heated up to the fusing point of the latter, one solid and three volatile products are obtained; the latter are ammonia, sulphuretted hydrogen, and sulphuret of carbon; the solid body is melam, mixed with chloride of potassium, which may be removed by washing with water.

Melam is a whitish-gray powder, insoluble in water, alcohol, and ether. It is dissolved and decomposed by long boiling in solution of potassa. Boiling nitric and sulphuric acids dissolve it, and their solutions treated by alcohol produce a precipitate of *ammelide*; but if boiled for several hours, with the occasional addition of water, the melam is wholly transmuted into cyanuric acid and ammonia. Melam is soluble in dilute hydrochloric and nitric acid, and converted into *ammeline* and *melamine*; the same products are obtained by continued boiling in solution of caustic potassa. When fused with hydrate of potassa, it is transformed into cyanate of potassa and gaseous ammonia. By the action of heat it is resolved into mellon and ammonia.

To the above statement, Liebig adds the following explanatory equations:

The ultimate elements of 8 atoms
of sulphocyanuret of ammonium } $16\text{ car} \quad 16\text{ n} \quad 32\text{ h} \quad 16\text{ s}$
 $8(\text{cy} + 2\text{ s}) + (\text{n} + 4\text{ h})$ are

These are resolved by heat into

1 atom of melam	12 car	11 n	9 h	
5 " of ammonia		5 n	15 h	
4 " bisulphuret of carbon . .	4 car			8 s
8 " sulphuretted hydrogen .			8 h	8 s
	<hr/>	<hr/>	<hr/>	<hr/>
	16 car	16 n	32 h	16 s

And as regards the conversion of 1 atom of melam and 6 of hydrate of potassa into 6 atoms of cyanate of potassa and 5 of ammonia,

The ultimate elements of } 1 atom of melam are	12 <i>car</i>	11 <i>n</i>	9 <i>h</i>		
6 atoms of hydrate of potassa .			6 <i>h</i>	12 <i>o</i>	6 <i>po</i>
	13 <i>car</i>	11 <i>n</i>	15 <i>h</i>	12 <i>o</i>	6 <i>po</i>

Resolved by fusion into

6 atoms of cyanate of potassa .	12 <i>car</i>	6 <i>n</i>		12 <i>o</i>	6 <i>po</i>
5 „ ammonia		5 <i>n</i>	15 <i>h</i>		
	12 <i>car</i>	11 <i>n</i>	15 <i>h</i>	12 <i>o</i>	6 <i>po</i>

MELAMIN. ($6\text{ car} + 6\text{ n} + 6\text{ h}$.)—Liebig thus designates a salifiable base, produced as above stated by the action of alkalis and dilute acids on melam: it is one of the most highly azotised compounds with which we are acquainted. To obtain it, melam (procured by the distillation of a mixture of 1 part of sulphocyanuret of potassium, and 2 of sal-ammoniac, and washed to free it from chloride of potassium) is boiled in a solution of 1 part of hydrate of potassa in 20 of water, till the turbid liquor becomes clear; it is then evaporated by a gentle heat, till small brilliant crystals form in it, when it is set aside, and on cooling the whole of the melamin separates. It is purified by recrystallization.

Melamin forms anhydrous rhomboidal octoëdra, transparent and colourless, or slightly yellow: very sparingly soluble in cold water, and more soluble, but slowly so, in hot water. It is insoluble in alcohol and in ether. Its aqueous solution has a bitter taste, and is without action upon vegetable colours. Dry melamin fuses at a high temperature, and sublimes almost without decomposition; a small portion of it is, however, resolved into mellon and ammonia.

Concentrated nitric and sulphuric acids decompose melamin with the aid of heat into ammonia and ammelide, or ammeline. Fused with hydrate of potassa, the elements of 3 atoms of water combine with it, and transform it into 3 atoms of ammonia which escape, and 3 atoms of cyanic acid which remain in combination with the potassa.

The ultimate elements of } 1 atom of melamin are	6 <i>car</i>	6 <i>n</i>	6 <i>h</i>		
3 atoms of hydrate of potassa			3 <i>h</i>	6 <i>o</i>	3 <i>po</i>
	6 <i>car</i>	6 <i>n</i>	9 <i>h</i>	6 <i>o</i>	3 <i>po</i>

Resolved by fusion into

3 atoms of cyanate of potassa.	6 <i>car</i>	3 <i>n</i>		6 <i>o</i>	3 <i>po</i>
3 „ ammonia		3 <i>n</i>	9 <i>h</i>		
	6 <i>car</i>	6 <i>n</i>	9 <i>h</i>	6 <i>o</i>	3 <i>po</i>

Melamin combines with dilute acids to form crystallizable salts, all of which, except the double salts, have an acid reaction. The nitrate, phosphate, and oxalate, are less soluble than melamin; the acetate and

formiate are very soluble: it precipitates a part of magnesia from its solutions, and forms a double salt with the residue; in the same way it decomposes the salts of all the common metals. It combines directly with the anhydrous hydracids. All the salts of melamin with the oxyacids, contain an atom of water, like the corresponding salts of ammonia, and cannot exist without it. It forms double basic salts in which this atom of water is replaced by an equivalent of metallic oxide.

AMMELIN. ($6\text{ car} + 5\text{ n} + 5\text{ h} + 2\text{ o.}$)—A product of the decomposition of melam and melamin by acids and alkalis. When melamin is prepared by decomposing melam by a solution of caustic potassa, a liquor is obtained, which, after having deposited the whole of the melamin which it held in solution, still retains ammeline dissolved by the potassa, which is thrown down in the form of a white gelatinous precipitate by acetic acid. This precipitate is to be washed and re-dissolved in dilute nitric acid. This nitric solution yields, by evaporation, crystals of pure nitrate of ammeline. These crystals are again dissolved in dilute nitric acid, and from this solution carbonate of ammonia throws down perfectly pure ammeline, which may be washed and dried.

Ammeline may also be obtained by dissolving melam in weak and boiling hydrochloric acid; by evaporation crystals of hydrochlorate of ammeline and of melamin are obtained, which are to be re-dissolved in boiling water; from this solution ammeline is thrown down by caustic ammonia, and the remaining liquor yields crystals of hydrochlorate of melamin.

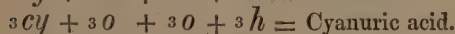
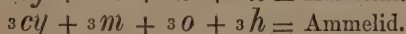
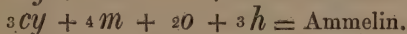
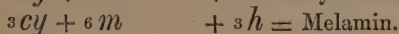
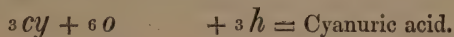
The precipitated ammeline forms brilliant white silky needles; it is insoluble in water, alcohol, and ether, but it dissolves in the caustic alkalis. Subjected to dry distillation, it affords a crystalline sublimate, ammonia, and a residue of pure mellon. With the acids it yields crystallizable salts. By the prolonged action of weak boiling acids, and of concentrated sulphuric acid, it is changed by the assumption of the elements of 1 atom of water: the products of this change are ammonia and ammeline. Fused with hydrate of potassa, it is transformed into ammonia and cyanate of potassa.

Ammeline is a very weak base, and only combines with the stronger acids, and never with the organic acids; its salts are crystalline, have an acid reaction, and are decomposed by water, which separates ammeline. On mixing nitrate of ammeline with the salts of many of the common metals, crystalline precipitates are formed, which are double basic salts, containing 1 atom of acid, 1 of ammeline, and 1 of metallic oxide. The oxyacid salts of ammeline contain, like the salts of ammonia, 1 atom of water: the double basic salts are anhydrous. Nitrate of ammeline crystallizes in large broad plates, or in long quadrangular prisms: it fuses when heated, and leaves ammeline as a residue, while nitric acid, and the products of the decomposition of nitrate of ammonia, are evolved.

AMMELID. ($12\text{ car} + 9\text{ n} + 9\text{ h} + 6\text{ o.}$)—A product of the decomposition of melam and ammeline by the concentrated acids: either of these is dissolved in concentrated sulphuric acid, the solution mixed with alcohol, and the precipitate formed washed with cold water till all traces of acid are removed. It is purified by dissolving it in dilute nitric acid,

and precipitating by carbonate of ammonia. Ammelid is a white powder, insoluble in water, alcohol, and ether; but soluble in alkalis and strong acids. With nitric acid it forms crystals which are decomposed by water. Exposed to the prolonged action of boiling dilute nitric or sulphuric acid, it is entirely resolved into ammonia and cyanuric acid. On adding slight excess of nitrate of silver to a boiling solution of ammelid in dilute nitric acid, and then ammonia till it forms a constant precipitate, white caseous flocculi are deposited on cooling, consisting of ammelid, in which the elements of an atom of water are replaced by those of oxide of silver.

THEORY OF THE COMPOSITION OF MELAMIN, AMMELIN, AND AMMELID.—In the following table Liebig attempts to explain the basic properties of melamin and ammelin, and the manner in which ammelid and cyanuric acid are derived from them. It is assumed that these substances contain the same radical as cyanuric acid, together with a combination of an equal number of atoms of nitrogen and hydrogen, which combinations we shall represent by m ; the formulæ will then stand as follows, $2m$ representing hn .



The cyanuric acid forms the beginning and end of the series. In melamin 6 atoms of oxygen are replaced by $6m$, and in ammelin 4 atoms by $4m$; both of these are saline bases; ammelid possesses no basic properties, and in it half the oxygen of the cyanuric acid is replaced by $3m$; lastly, when the whole of m is replaced by oxygen, the cyanuric acid again appears. The basic properties of these substances diminish, in proportion as the oxygen of the radical increases. Liebig says that the cyanuric acid may be compared to the phosphoric acid, and melamin to phosphuret of hydrogen, or to ammonia; inasmuch as ammonia and melamin combine directly with the hydracids; that is, without the intervention of water; but with the oxyacids an atom of water enters into the compound, where it plays the same part as in the salts of ammonia.

§ XII. BORON.

THIS substance was discovered in 1807, by Sir H. Davy, and in 1808 its properties were examined by Gay Lussac, and Thenard. (*Recherches Physico-Chimiques*.) It is obtained by heating in a copper tube two parts of potassium, with one of boracic acid previously fused and powdered. The fused matter is washed out of the tube with water, and the whole put upon a filter. The boron remains in the form of a brown insipid insoluble powder. According to Döbereiner (*Ann. de Ch. et Ph.*, ii. 214), one part of charcoal or lampblack, intensely heated in a gun-barrel, with nine parts of borax, previously fused, and in fine powder, produces a dis-

engagement of carbonic oxide, and a blackish mass results, which, after copious washings in boiling water, and once with hydrochloric acid, affords a greenish-black powder, having the characters of boron mixed with a little charcoal. The charcoal probably first reduces the soda, and the sodium decomposes the boracic acid; hence the produce of boron would probably be increased by adding to the borax half its weight of soda or potassa, and double the quantity of charcoal above-mentioned. According to Berzelius (*Ann. of Phil.*, xxx. 128), boron is most economically obtained by decomposing the borofluoride of potassium. This compound, dry and in powder, is heated in a porcelain crucible with potassium; the reduction goes on quietly, and the fused mass is triturated with water, by which the boron is separated, which is then washed upon a filter with a solution of hydrochlorate of ammonia, and afterwards with alcohol.

Boron is a very deep olive-coloured substance, infusible, inodorous, insipid, and a non-conductor of electricity. Its specific gravity exceeds 2. It is not acted upon by air, water, alcohol, ether, or oils. In the state of hydrate it long remains diffused through pure water, and passes through filters; but its precipitation is accelerated by saline solutions. It undergoes no change when heated in close vessels; but when nearly red-hot in the air, it takes fire and burns with difficulty into *boracic acid*. It is more easily oxidized by the action of nitric acid: the pure hydracids have no action upon it, but nitrohydrochloric acid converts it into boracic acid, and nitrohydrofluoric acid into fluoride of boron. At a high temperature it rapidly decomposes nitre, even with explosive violence; under the same circumstances, it also decomposes and deflagrates with the hydrate and carbonate of potassa: in the former case water is decomposed, and hydrogen evolved; in the latter, carbonic oxide is evolved in consequence of the decomposition of carbonic acid; in both cases borate of potassa is the result.

BORACIC ACID. (*bo + c o*) or *bo'*.—This, which is the only known compound of boron and oxygen, was first obtained by Homberg in 1702, and was used in medicine under the name of *sedative salt*. Its composition was demonstrated by Davy in 1807. It is usually obtained by dissolving the salt called *borax* in hot water, and subsequently adding half its weight of sulphuric acid; as the solution cools, white scaly crystals appear, which, when washed with cold water, are nearly tasteless, and which consist of boracic acid combined with about 40 per cent. of water, and retaining a little sulphuric acid, which it loses at a red heat; but inasmuch as such impure boracic acid attacks both metallic and porcelain crucibles, (for although neither sulphuric nor boracic acid separately injure platinum, the combination soon corrodes it,) this ignition cannot be effectually performed upon it, another method must be resorted to, which consists in decomposing a hot saturated solution of borax by hydrochloric acid; the hydrated boracic acid which falls as the liquid cools, may then be washed and dried, and safely heated in a platinum crucible, when it fuses into a hard transparent glass. Its specific gravity before fusion is 1.48; after fusion, about 1.8. At a white heat this acid slowly sublimes when exposed to air.

The *hydrated boracic acid*, is soluble in about 30 parts of cold, and 3 of boiling water: the latter solution deposits it in pearly scales as it cools: it is also soluble in alcohol, to the flame of which it communicates a green colour. It has little taste and feebly reddens vegetable blues; it renders turmeric brown, like an alkali. (FARADAY, *Quarterly Journal*, xi. 403.) The anhydrous acid becomes opaque when exposed to air; it is very fusible, and forms fusible combinations with many of the metallic oxides; hence, it is often used as a flux. When boracic acid is perfectly pure, it is deposited from its aqueous solution, not in scales, but in small prismatic crystals.

According to Davy, boron, when burned in oxygen, or acidified by nitric acid, combines with about 68 *per cent.* of oxygen; and with this, the theoretical estimate of Berzelius coincides: there is, however, a difference of opinion as to the equivalent of boron and that of the boracic acid; the analysis of Berzelius, Arfwedson, and Soubeiran, gives the proportion of the acid to that of the soda in *borate of soda* as 68 to 32, and assuming that salt as a compound of one equivalent of acid, and one of base, I have upon the authority of Gmelin, sanctioned by the above analysts, and by the composition of some of the other borates, adopted 68 as the equivalent of the *anhydrous boracic acid*; it will, therefore, consist of

					Berzelius	
Boron	. . .	1	. . .	20	. . .	29.41
Oxygen	. . .	6	. . .	48	. . .	70.59
						100.00
Boracic acid		1		68		100.00

And the *hydrated prismatic crystals* will consist of

					Berzelius.	
Anhydrous boracic acid	. . .	1	. . .	68	. . .	55.74
Water	„	6	. . .	54	. . .	44.26
						100
Hydrated boracic acid		1		122		100.00

These crystals lose 3 atoms of water when dried at 212°.

NATIVE BORACIC ACID, occurs among the volcanic products of the Lipari Islands, whence it has been collected for the manufacture of borax; it also exists in the hot springs of that district, and in those of Sasso, in the Florentine territory, whence the term *sassolin* applied to it by some mineralogists. It also occurs in *Datolite*, *Boracite*, and some other minerals, and in native *Borax*. An account of the Tuscan *lagoni*, whence large quantities of this acid are obtained, is given by Dumas (*Chim. App. aux Arts*, i. 379).

BORACIC ACID AND AMMONIA. BORATE OF AMMONIA. (A + 60'.)—According to L. Gmelin, a neutral borate of ammonia is obtained by dissolving boracic acid in slight excess of warm solution of ammonia; the temperature rises, and by slow cooling opaque rhombic octoëdra are deposited, which effloresce by exposure to air, and give off ammonia; they are soluble in 12 parts of cold water and the solution when heated is converted into *biborate*. This salt consists of

					L. Gmelin.	Soubeiran.	Arfwedson.			
Ammonia	. . .	1	. . .	17	. . .	12.5	. . .	13.544	. . .	12.88
Boracic acid	. . .	1	. . .	68	. . .	52.31	. . .	51.0	. . .	50.000
Water	. . .	5	. . .	45	. . .	34.61	. . .	36.5	. . .	36.452
Borate of ammonia		1		130		100.00		100.0		99.996
										100.00

BIBORATE OF AMMONIA. ($A + 2bo'$).—This salt is formed by saturating warm solution of ammonia by boracic acid, and slow evaporation: it yields transparent, irregular, six-sided prisms, at first tasteless, then hot and bitter, and having alkaline reaction on test paper. It dissolves in eight parts of cold water, and gives out ammonia when heated. L. Gmelin (*Handbuch*), Soubeiran (*Jour. de Pharm.*, xi. 34), Arfwedson (POGGEND., ii. 130). This salt contains

				Arfwedson.	L. Gmelin.
Ammonia	1	17	7.87	7.9	5.9
Boracic acid	2	136	62.96	64.0	63.4
Water	7	63	29.17	28.1	30.7
Biborate of ammonia	1	216	100.00	100.0	100.0

CHLORIDE OF BORON. ($bo + ^6c$).—Sir H. Davy first observed the combustion of boron in chlorine, and afterwards Berzelius found that on passing dry chlorine over heated boron, or over a red-hot mixture of dry boracic acid and charcoal, a permanent gas was formed which might be freed from chlorine by passing it through mercury. This gas has a pungent odour; it is colourless, fumes in contact of air, is rapidly absorbed by water, soluble in alcohol, and forms a liquid compound with ammonia. (*Ann. of Phil.*, xxvi. 129.) Its specific gravity according to Dumas is 3.942. When absorbed by water it forms boracic and hydrochloric acid.

It consists of

				Dumas.
Boron	1	20	8.5	9.29
Chlorine	6	216	91.5	90.71
Chloride of boron	1	236	100.0	100.00

IODIDE and BROMIDE OF BORON are unknown.

FLUORIDE OF BORON. FLUOBORIC ACID. ($bo + ^6f$).—In the hope of obtaining anhydrous fluoric acid, Gay Lussac and Thenard heated a mixture of vitrified boracic acid and fluor-spar; the result was not as they had anticipated, but a peculiar gaseous compound was obtained, to which they gave the name of *fluoboric acid*. (*Mem. d'Arcueil*, ii. 317.) Dr. John Davy obtained the same gas, not, however, perfectly pure, by heating in a glass retort, over a lamp, a mixture of one part of vitrified boracic acid, two parts of finely-powdered fluor-spar (fluoride of calcium), and twelve parts of sulphuric acid. (*Phil. Trans.*, 1812.) It is most probable that, in obtaining this gas, the oxygen of the boracic acid combines with the calcium of the fluor-spar to form oxide of calcium or lime, and that the boron and fluorine unite to produce the gas.

Fluoboric gas, according to Dr. Davy, has a specific gravity = 2.371, according to Dumas = 2.31; it is colourless, of a pungent odour, highly deleterious to respiration, and extinguishes flame. It strongly reddens litmus; and when bubbles of it are allowed to escape into the air, they produce a remarkable dense and white fume, in consequence of their eager attraction for, and combination with, aerial moisture. Water takes up 700 times its volume of the gas, increasing in volume and density, and forming a caustic and fuming solution, in which Berzelius found boracic and hydrofluoric acids in combination, (*borohydrofluoric acid*;) it would seem, therefore, that fluoboric gas decomposes water, and that the hydrogen of the water unites to the fluorine to form hydrofluoric acid,

and the oxygen to the boron, to form boracic acid. When the solution is concentrated, the hydrofluoric and boracic acids again decompose each other, and the original compound is reproduced. Neither the gas nor the liquid acid act upon glass, but they speedily decompose almost all organic substances: a piece of paper introduced into the gas, standing in a tall jar, over mercury, causes its rapid absorption, and becomes charred as if burned, in consequence of the abstraction of the elements of water. When potassium is heated in fluoboric gas, it burns, and a brown compound results, consisting of boron and fluoride of potassium: the latter may be dissolved in water, and pure boron remains. Regarding fluoboric gas as a binary compound, it consists of

				Berzelius.	Vols.	Sp. Gr.
Boron	1	20	16	16.24	1	1.3866
Fluorine	6	108	84	83.76	3	7.7572
	<u>1</u>	<u>128</u>	<u>100</u>	<u>100.00</u>	<u>4*</u>	<u>2.2809</u>

FLUOBORATE OF AMMONIA.—Fluoboric acid and ammonia condense each other apparently in three proportions. If *one* measure of the acid gas be admitted to *one* of ammonia, in a jar over mercury, complete condensation ensues, and a solid compound results, which sublimes without decomposition when gently heated. It consists probably of

				J. Davy.
Ammonia	2	34	21	20
Fluoboron	1	128	79	80
	<u>1</u>	<u>162</u>	<u>100</u>	<u>100</u>

LIQUID SUBFLUOBORATE OF AMMONIA.—*One* measure of fluoboric gas with *two* of ammoniacal gas, condensed each other into a colourless liquid, which, when heated, or exposed to air, lost ammonia, and became converted into the former solid. This liquid compound consists therefore of

				J. Davy.
Ammonia	4	68	34.69	33
Fluoboron	1	128	65.31	67
	<u>1</u>	<u>196</u>	<u>100.00</u>	<u>100</u>

Dr. Davy also found that a compound might be formed of 1 volume of fluoboric gas, and 3 of ammoniacal gas, or of 1 proportional of the former, and 6 of the latter, and which, in its chemical properties, closely resembled the preceding.

SULPHURET OF BORON.—When boron is strongly heated in sulphur-vapour, it burns and produces an opaque white compound, which by the contact of water yields boracic acid and sulphuretted hydrogen. (BERZELIUS.)

* In this calculated result, which nearly coincides with experiment, it is assumed that the specific gravity of boron vapour is 20 times that of hydrogen, and that the volume of fluorine which represents its specific gravity in reference to hydrogen is, as is the case with oxygen, equal to two equivalents.

SUCH are the general properties of the simple non-metallic substances, and of their mutual combinations; they have been described in the order suggested at page 350, and I trust that the principles of nomenclature which are there adverted to will now be intelligible, and that the arrangement, adopted in respect to them and their numerous compounds, will be thought sufficiently perspicuous and convenient to justify the application of a similar method to the *metals*, and to the multifarious combinations which that important class of substances form with the bodies which have been described in this chapter. I have already observed, that, strictly speaking, the basis of Silica, under the name of *silicon*, should have been placed among the non-metallic elements, and that the analogies which it bears to *boron* are such, as to justify its dismissal from the metals: but others of its characters have been but imperfectly examined; and, if general analogies are made the basis of our arrangements, it would not be difficult to show that, in many other cases, the line of demarcation between the non-metallic and metallic bodies, is so indistinct, as to render it probable that they may gradually merge into each other, and that the distinctive characters by which it has been attempted to separate them, are not well-founded: these matters will be more evident, when the history of the individual metals is examined; thus, the striking analogy that subsists between sulphur and arsenic, is such, as closely to approximate those substances; and some of the other acidifiable metals are, by a similar analogy, related to arsenic; and, on the other hand, carbon approximates so closely in certain of its characters, to those considered appropriate to the metals, as, in the opinion of some, to justify its being placed among them: in short, the more we examine into the details of our artificial arrangements, the less consistent do we in general find them with nature; so that they should always be regarded as merely tending to the convenience of description and discussion, and not as possessing any further claims upon our consideration. Hence, I have not thought it worth adverting, in detail, to the opinions of contemporary writers upon this subject, or enumerating the grounds upon which they have contrived plausibly to arrange the subjects of chemistry in an order extremely at variance with that which is here adopted. To describe those substances first, which, in the common acceptance of the term, are most important, which are of most frequent occurrence, and most influential in the majority of chemical phenomena, and to associate the description of compounds with those of their elements, seems to me to be the system which least perplexes the student, and is, therefore, that upon which the preceding and succeeding portions of this work are founded.

CHAPTER VI.

OF THE METALS, AND THEIR COMBINATIONS.

THE metals constitute a numerous and important class of simple substances. They are forty-three in number, and are enumerated in the following table with their equivalent numbers and symbols annexed.

	Equiv.	Symbol.		Equiv.	Symbol.
1. Gold	200	<i>aur.</i>	23. Palladium	54	<i>pal.</i>
2. Silver	108	<i>ag.</i>	24. Rhodium	52	<i>rh.</i>
3. Copper	32	<i>cu.</i>	25. Iridium	96	<i>ir.</i>
4. Iron	28	<i>fe.</i>	26. Osmium	100	<i>os.</i>
5. Mercury	200	<i>hg.</i>	27. Cerium	48	<i>ce.</i>
6. Tin	58	<i>sta.</i>	28. Potassium	40	<i>po.</i>
7. Lead	104	<i>pl.</i>	29. Sodium	24	<i>so.</i>
8. Zinc	32	<i>zn.</i>	30. Lithium	8	<i>li.</i>
9. Bismuth	72	<i>bi.</i>	31. Barium	69	<i>ba.</i>
10. Antimony	65	<i>an.</i>	32. Calcium	20	<i>cal.</i>
11. Arsenic	38	<i>ar.</i>	33. Strontium	44	<i>str.</i>
12. Cobalt	30	<i>cob.</i>	34. Magnesium	12	<i>mag.</i>
13. Platinum	99	<i>pla.</i>	35. Silicium	8	<i>si.</i>
14. Nickel	28	<i>nic.</i>	36. Alumium	26	<i>al.</i>
15. Manganese	28	<i>man.</i>	37. Yttrium	32	<i>yt.</i>
16. Tungsten	100	<i>tu.</i>	38. Glucinum	18	<i>gl.</i>
17. Tellurium	32	<i>tel.</i>	39. Zirconium	22	<i>zir.</i>
18. Molybdenum	48	<i>mol.</i>	40. Cadmium	56	<i>cad.</i>
19. Uranium	217	<i>urnm.</i>	41. Thorium	60	<i>th.</i>
20. Titanium	24	<i>ti.</i>	42. Vanadium	68	<i>va.</i>
21. Chromium	28	<i>chr.</i>	43. Lantium	?	<i>lan.</i>
22. Columbium	185	<i>col.</i>			

Of these metals the first seven were known in very remote ages. The ancients designated them by the names of the planets, to which they were supposed to have some mysterious relation; and each was denoted by a particular symbol, representing both the metal and the planet. (In respect to the origin and application of these symbols, see BECKMANN'S *History of Inventions*.)

Gold	was the Sun,	and was thus represented	☉
Silver	... Moon	...	☾
Mercury	... Mercury	...	☿
Copper	... Venus	...	♀
Iron	... Mars	...	♂
Tin	... Jupiter	...	♃
Lead	... Saturn	...	♄

Zinc was not known to the ancients, though they were probably acquainted with its ores, and with their property of forming brass when

fused with copper. (PLINY, lib. xxxiv., cap. 2 and 10.) The word *Zinc* first occurs in the writings of Paracelsus, who died in 1541. Bismuth is mentioned in the *Bermannus* of Agricola, written about 1530. Antimony was first obtained in its pure state by Basil Valentine towards the end of the fifteenth century; it is described in his *Currus Triumphalis Antimonii*. Arsenic and Cobalt were discovered by Brandt in 1733 (*Acta Upsal.* 1733 and 1742); the ores were known at a much earlier period. Platinum was first recognised as a peculiar body in 1741, by Mr. Charles Wood, Assay-Master in Jamaica (*Phil. Trans.*, vol. xlv.) In 1751, the distinctive characters of Nickel were shown by Cronstedt (*Stockholm Transactions*), and Manganese was obtained by Gahn in 1774 (BERGMAN'S *Opuscula*, vol. ii.) Tungsten was discovered by MM. Delhuyart, in 1781 (*Mémoires de Toulouse*). Tellurium and Molybdenum by Müller and Hielm, in 1782 (CRELL'S *Annals*, 1790 and 1798). Uranium by Klaproth in 1789. Titanium by Gregor, in 1789 (*Jour. de Phys.*, xxxix.) Chromium by Vauquelin, in 1797 (*Ann. de Ch.*, vol. xxv.) In 1802, Hatchet discovered Columbium (*Phil. Trans.*) Palladium and Rhodium were discovered by Wollaston; and Iridium and Osmium by Tennant, all in 1803 (*Phil. Trans.*) Cerium was announced in 1804, by Hisinger and Berzelius (GEHLEN'S *Journal*, ii.) Potassium and Sodium were discovered in 1807, by Davy, whose experiments also led to the discovery of the metallic nature of the ten following bodies (*Phil. Trans.*) Stromeyer discovered Cadmium in 1818 (*Ann. of Phil.*, xiii.) Thorium was discovered by Berzelius in 1829 (POGGEND., *Ann.*, xvi.), Vanadium by Sefström in 1830 (*Ann. de Ch. et Ph.*, xlvi.), and Lanthanum by Mosander in 1838.

Metals are chiefly found in the earth in *veins* which traverse the granitic, schistose, and limestone rocks; they also occur, although comparatively rarely, in rounded and detached fragments and nodules, disseminated through certain alluvial and diluvial strata. They seldom occur in an uncombined state, but almost always united to other substances, as in the following classes:—

i. *Native Metals* are those which occur pure or alloyed, such as platinum, rhodium, iridium, osmium, gold, silver, mercury, copper, antimony, arsenic, and tellurium.

ii. *Metals combined with simple non-metallic substances.* The compounds belonging to this class are the *native metallic oxides*, and *native chlorides*; *iodides* and *bromides* are extremely rare; and there are few *fluorides*. The *native metallic sulphurets* are a numerous and important series of ores. The *seleniurets* are rare. There are no native carburets, hydrurets, phosphurets, nor borurets.

iii. *Metals in combination with acids; Metallic Salts.* Of these the most common are the *native carbonates*, *sulphates*, and *phosphates*: there are a few *native borates*; and a few species belong also to this class in which the oxide is united to a *metallic acid*: such as the *native arseniates*, *chromates*, *tungstates*, *molybdates*, and *vanadates*.

PROPERTIES OF THE METALS.—*Opacity, &c.* The metals, as a class, are characterized by *opacity*, and a peculiar *lustre*. Their *opacity* is such, that even when extended into very thin leaves, they generally trans-

mit no light; silver-leaf, only one one-hundred-thousandth of an inch in thickness, is perfectly opaque. Gold, however, when beaten out into leaves one two-hundred-thousandth of an inch in thickness, transmits green rays of light; and it is probable that thin films of other metals transmit certain rays of light. Their lustre depends upon their great power of reflecting light, in consequence of their opacity. They are excellent conductors of heat and of electricity. (See pages 155 and 245.)

The polished metals are very imperfect radiators and receivers of heat (page 211); but they are excellent reflectors both of light and heat, and hence their peculiar fitness for the construction of mirrors.

Whenever the polish of the metallic surface is impaired, its power of reflecting heat suffers a proportionate diminution, while its power of absorbing, and also of radiating heat, is proportionably increased. (See page 206.)

Crystallization. The greater number of the metals are susceptible of assuming the crystalline form. With many this may be effected by fusion and slow cooling, and especially by suffering a ladle, or crucible, filled with the melted metal, to concrete externally, and then perforating the solid crust, and pouring out the liquid interior; the cavity so formed will then be lined with crystals: this mode of proceeding answers extremely well with bismuth, which furnishes a singular congeries of cubic crystals (p. 113). When the metals are precipitated by each other, they often crystallize during their deposition, as is seen in the precipitation of silver by mercury, and in that of lead by zinc. A stick of phosphorus immersed in a solution of silver becomes incrustated with beautiful metallic crystals, which, after some time, perfectly encase the phosphorus. Gold is occasionally deposited in a crystalline form, from its ethereal solutions. Some curious facts relating to this subject, will be found in a paper by Professor Daniell, "On certain phenomena resulting from the action of Mercury upon different Metals." (*Royal Instit. Journal*, i. 1.) During the electrolysis of metallic solutions, especially where low powers are employed, beautiful metallic crystals are also occasionally obtained.

Specific Gravity. There is the greatest difference in the *specific gravity* of the different metals, the heaviest and lightest solids being included in the list. Their specific gravity is also in some instances a little increased by hammering, rolling, and some other mechanical processes by which they are permanently compressed.

The principal metals, arranged according to their specific gravities, stand as follows (Temp. 60°, Water = 1):—

Platinum	20.98	Nickel	8.27
Gold	19.258	Iron	7.78
Iridium	18.680	Molybdenum	7.40
Tungsten	17.50	Tin	7.30
Mercury	13.568	Zinc	7.00
Palladium	11.50	Manganese	6.85
Lead	11.35	Antimony	6.70
Silver	10.47	Tellurium	6.10
Bismuth	9.80	Arsenic	5.8
Uranium	9.00	Titanium	5.3
Copper	8.89	Sodium	0.972
Cadmium	8.60	Potassium	0.865
Cobalt	8.53		

Malleability. Among the metals, some are *malleable*, others *brittle*; hence the ancient division into *perfect* and *semi-metals*. Common gold-leaf is not more than $\frac{1}{200000}$ th of an inch in thickness, and five grains are sufficient to cover a surface of more than 270 square inches. This capacity of being extended by the hammer, belongs to the following metals:—

Gold	Tin	Lead	Nickel	Sodium
Silver	Cadmium	Zinc	Palladium	Frozen Mercury.
Copper	Platinum	Iron	Potassium	

Ductility. The malleable metals are also *ductile*; that is, they admit of being drawn out into wires. A grain of gold may be drawn into 500 feet of wire; and by enveloping it in silver, Dr. Wollaston found that it might be so extended, as that 700 feet weighed only one grain; in thickness, therefore, not exceeding $\frac{1}{300000}$ th of an inch. The coating of silver was removed by dilute nitric acid. In the same way he produced platinum wire of similar tenuity. (*Phil. Trans.*, 1813.) The metals are arranged according to ductility as follows:—

Gold	Iron	Tin	Palladium
Silver	Copper	Lead	Cadmium.
Platinum	Zinc	Nickel	

Tenacity. Different metallic wires are possessed of different degrees of *tenacity*, by which is meant the power of supporting a weight without breaking. According to the experiments of Guyton Morveau, the following are the weights sustained by wires 0·787 of a line in diameter (*Ann. de Ch. et Ph.*, LXXI.):—

	lbs. avoir.	dec. parts.		lbs. avoir.	dec. parts.
A wire of iron supports	549	250	A wire of gold supports	150	753
„ copper	302	278	„ zinc	109	540
„ platinum	274	320	„ tin	34	630
„ silver	187	137	„ lead	27	621

Brittleness. The following metals are brittle, and most of them may even be reduced to powder:—

Antimony	Cerium	Columbium	Tellurium	Uranium
Arsenic	Chromium	Manganese	Titanium	Rhodium.
Bismuth	Cobalt	Molybdenum	Tungsten	

Hardness. Few of the metals, when pure, are very *hard*, and many so soft as to yield to the nail. In the following table, some of the metals are arranged in the order of their hardness. (DUMAS.)

Titanium	} Harder than steel.	Chromium	} Scratch glass.
Manganese		Rhodium	
Platinum		Nickel	
Palladium		Cobalt	
Copper		Iron	} Scratched by glass.
Gold	} Scratched by calc-spar.	Antimony	
Silver		Zinc	} Scratched by the nail.
Tellurium		Lead,	
Bismuth		Potassium	
Cadmium		Sodium	} Soft as wax (at 60°).
Tin		Mercury,	
			Liquid.

Elasticity and sonorousness belong to the hardest metals only, and are most evident in certain alloys.

Odour and Taste. There are several of the metals which have a peculiar odour, especially when they are rubbed, or their temperature otherwise slightly elevated; this is more especially the case with copper, iron, and tin. It has been supposed that these metals owe their smell and taste to some foreign matter, and possibly electricity may be concerned; yet many of the most oxidable metals are entirely destitute both of taste and odour.

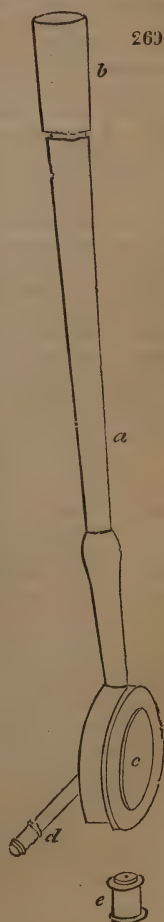
Fusibility*. The metals are all susceptible of fusion by heat, but the temperatures at which they liquify are extremely various. Mercury is fluid at common temperatures, and requires to be cooled to -39° before it congeals. Potassium melts at about 140° , and sodium at 200° ; tin at 450° ; lead at 600° ; zinc at 700° ; and antimony at 800° . Silver, gold, and copper, require a bright cherry-red heat; iron, nickel, and cobalt, a white heat; manganese and palladium, an intense white heat; molybdenum, uranium, tungsten, and chromium, are only very imperfectly agglutinated at the highest temperatures of our furnaces; and titanium,

* In the examination of the effects of heat upon metallic and mineral substances, the *blowpipe* is a most useful and necessary auxiliary to our other operations; it affords a simple and convenient means of heating to a very high degree, and almost instantaneously, any substance sufficiently small to be enveloped in its flame; and the experienced eye is thus frequently enabled to anticipate, with much precision, the nature of the substance submitted to experiment. There are numerous forms of the blow-pipe, among which, that represented in fig. 269 is perhaps the most convenient. It consists of a brass-tube *a*, with an ivory mouth-piece *b*; the other end of the tube terminates in a circular box, from which issues the small tube *d*, moveable in any direction round the centre *c*, by which any degree of obliquity may conveniently be given to the flame; *e* is a brass jet which fits upon the tube *d*.

The following observations respecting the use of the blow-pipe, and its action upon several substances, are extracted from Mr. CHILDREN'S *Essay on Chemical Analysis*; a work from which the student may derive much valuable information.

A continued stream of air is absolutely essential, to produce which, without fatigue to the lungs, an equable and uninterrupted inspiration must be maintained by inhaling air through the nostrils, whilst that in the mouth is forced through the tube by the compression of the cheeks. A little practice will make this operation easy, but at first considerable lassitude is generally experienced in the buccinator muscles. Upon this subject, see FARADAY'S *Manipulation*, s. iv. After habit has rendered the operation familiar, a current may be kept up for ten or fifteen minutes, without inconvenience. A large wax-candle supplies the best flame, which being urged by the blast, exhibits two distinct figures; the *internal* flame is conical, blue, and well defined, at the apex of which the most violent degree of heat is excited: the *external* is red, vague, and undetermined, and of very inferior temperature to the former.

The substance to be submitted to the action of the blow-pipe, which should not be larger than a small pepper-corn, must be supported either on charcoal, or a slip of platinum or silver foil, or be held in a pair of platinum pincers. In the first case it may be placed in a cavity in the charcoal, and another piece laid over it to prevent its being carried off by the blast. The metallic supports are used when the subject of the experiment is



cerium, osmium, iridium, rhodium, platinum, and columbium, require the intense heat produced by an inflamed current of oxygen and hydrogen, or that of Voltaic electricity. Arsenic volatilizes before it fuses; but in general, at higher temperatures than that required for their fusion, the metals are volatile, and many of them may be distilled in close vessels. Mercury, cadmium, arsenic, potassium, sodium, tellurium, and zinc, are volatile at a red heat. Gold and silver are converted into vapour when exposed to the intense heat of the focus of a burning lens; and several of the other metals boil and evaporate under similar circumstances. It is probable that this would happen to all of them, if raised to sufficiently high temperatures.

intended to be exposed to the action of heat only, and might be altered by contact with the charcoal. If a very intense heat be required, the foil may be laid on charcoal. Salts and volatile substances are to be heated in glass tubes, closed at one end, and enlarged according to circumstances, so as to form small matrasses.

The exterior flame should first be directed on the substance, and when its action is known, then the interior blue flame. Notice should be taken, whether the matter decrepitates, splits, swells up, liquifies, boils, vegetates, changes colour, smokes, is inflamed, becomes obedient to the magnet, &c.: when the action of heat alone has been ascertained, it will be necessary to examine what further change takes place, by fusing it with various fluxes, and also whether it be capable of reduction to the metallic state.

The three most useful fluxes are, the triple phosphate of soda and ammonia, carbonate of soda, and borax. These are to be kept ready pulverized, and when used, a sufficient quantity may be taken up by the moistened point of a knife; the moisture causes the particles to cohere, and prevents their being blown away, when placed on the charcoal. The flux must be melted into a clear bead, and the substance then placed on it, and submitted, first to the action of the exterior, and then to that of the interior, flame. The appearances which ensue must be observed; as, 1st. If the substance be dissolved, and whether with or without effervescence. 2nd. The transparency, and colour of the glass whilst cooling. 3rd. The same circumstances when cold. 4th. The nature of the glass formed by the exterior flame. 5th. Also by the interior flame. 6th. The particular appearances with each of the fluxes.

Carbonate of soda does not form a bead on charcoal, but with a certain degree of heat is absorbed; it must therefore be added in very small quantities, and a gentle heat used at first, which will promote combination without the absorption of the alkali. Some minerals combine readily with very small portions of soda, but difficultly if more be added, and are absolutely infusible with it in great excess; and when the substance has no affinity for this flux, it is absorbed by the charcoal, and no combination ensues. When the mineral contains sulphur or sulphuric acid, the glass acquires a deep-yellow colour, which by the light of a lamp appears red, as if produced by copper. If the glass bead become opaque as it cools, so as to render the colour indistinct, it should be broken, and a part of it mixed with more of the flux, till the colour becomes purer, and distinct. To make the colour more perceptible, the bead may be flattened whilst soft, or drawn-out to a thread.

If it be wished to *oxidate* a metallic substance, combined with either of the fluxes, the glass is first heated intensely, and when fused, gradually withdrawn from the point of the blue flame, and the operation repeated as often as necessary, using a jet of large aperture. The addition of a little nitre also assists the oxidation. For the *reduction* of metallic oxides, the glass bead is to be kept in fusion on charcoal, as long as it remains on the surface and is not absorbed, that the metallic particles may collect into a globule. It is then to be fused with an additional quantity of soda, which will be absorbed by the charcoal, and the spot where the absorption has taken place strongly ignited by a tube with a small aperture. By continuing the ignition, the portion of metal which was not previously reduced will now be

The following table of the fusibility of the metals has been drawn up by Dr. Turner. (*Elements of Chem.*)

		Fahrenheit.	
Fusible below a red heat.	Mercury	-39°	Different Chemists.
	Potassium	136°	Gay Lussac and
	Sodium	190°	Thenard.
	Tin	442°	Crichton.
	Bismuth	497°	
	Lead	612°	
	Tellurium: rather less fusible than lead		Klaproth.
	Arsenic, undetermined.		
	Zinc	773°	Daniell.
	Antimony, little below redness		
	Cadmium	442°	Stromeyer.
	Silver	1873°	Daniell.
Infusible below a red heat.	Copper	1996°	
	Gold	2016°	
	Cobalt; rather less fusible than iron.		
	Iron, cast	2786°	Daniell.
	Iron, malleable	} require the highest heat of a smith's forge.	
	Manganese		
	Nickel, nearly the same as cobalt.		
	Palladium	} Almost infusible, and not to be procured in buttons by the heat of a smith's forge, but fusible before the oxyhydrogen blowpipe.	
	Molybdenum		
	Uranium		
	Tungsten		
	Chromium		
	Titanium		
	Cerium		
	Osmium		
	Iridium		
	Rhodium		
	Platinum		
	Columbium		

ACTION OF OXYGEN.—When the metals are exposed at ordinary temperatures to the action of oxygen, or of common air, which produces analogous, though less powerful effects, they are very differently affected. If the gas be perfectly dry, few of them suffer any change, unless heated in it; they then lose their metallic characters, and form an important series of compounds, the *metallic oxides*. A few of the metals resist the action of heat and air so completely, that they may be kept in fusion in an open crucible for many hours without undergoing change. This is the case with platinum and gold; hence they and a few others were called *noble metals*: by passing a strong electric discharge through them,

brought to the metallic state, and the process may be assisted by placing the bead in a smoky flame, so as to cover it with a soot that is not easily blown off.

The beads which contain metals frequently have a metallic splendour, which is most easily produced by a gentle, fluttering, smoky flame, when the more intense heat has ceased. With a moderate heat the metallic surface remains; and by a little practice it may generally be known whether the substance under examination contains a metal or not.

But the glass of borax alone sometimes assumes externally a metallic appearance. When the charcoal is cold, that part impregnated with the fused mass should be taken out with a knife, and ground with distilled water in an agate mortar. The soda will be dissolved; the charcoal will float, and may be poured off; and the metallic particles will remain in the water, and may be examined. In this manner most of the metals may be reduced.

when drawn into very fine wire, they are reduced to the state of impalpable powder, which is sometimes regarded as an oxide; but the appearance ensues in hydrogen as well as in common air, and the oxides of those metals are reducible by heat alone: the appearance, therefore, is probably referable to minute mechanical division only. Other metals readily absorb oxygen when exposed to a temperature approaching a red heat; as iron, mercury, nickel, &c.; others absorb it when in fusion, as lead, tin, antimony, &c.; others at lower, or even at common temperatures, as arsenic, manganese, sodium, potassium, &c. The mutual action, however, of metals and oxygen is apparently much interfered with by their aggregation, for some of them, which under ordinary circumstances are only slowly oxidized by exposure to air and heat, are rapidly acted on when in very fine mechanical division, even at common temperatures; and this would probably be found more generally the case, had we the means of reducing them to extremely fine powder.

That the metals have different attractive powers in regard to oxygen is shown by the circumstance of one metal being oxidized at the expense of another: thus the oxide of mercury, heated with metallic iron, produces metallic mercury and oxide of iron; potassium, heated with oxide of manganese, becomes oxidized, and metallic manganese is obtained. Upon the same principle, solutions of metallic oxides in the acids may often be reduced to the metallic state by the immersion of other metals. Mercury thus decomposes nitrate of silver; copper decomposes nitrate of mercury; and iron decomposes nitrate of copper. In these cases of metallic precipitation, electricity becomes active the moment that the deposition commences; the precipitating or reducing metal being positive, and that which is precipitated, or reduced, negative. Very beautiful crystalline deposits may thus often be obtained, as where silver is precipitated by mercury, and lead by zinc. Metals which are in this way difficultly thrown down from their solutions in acids, are sometimes easily obtained from their solutions in alkalis, as for instance tungsten and tin.

Many of the metallic oxides are reduced, when in solution, by the protosalts of iron and tin, which by abstracting oxygen pass into the state of persalts, and throw down the reduced metal in a pulverulent form. The protosalts of iron are in these cases preferable to those of tin, inasmuch as the resulting peroxide of iron is retained in solution, and the precipitated metal is pure; but the peroxide of tin often falls along with the reduced metal, in consequence of its difficult solubility in most of the acids.

Some of the oxides are decomposed by mere exposure to heat, as those of platinum, gold, silver, and mercury: others require the joint action of heat, and some substance having a high attraction for oxygen, such as charcoal. Thus when oxide of lead is heated with charcoal, carbonic acid gas is evolved, and metallic lead obtained. This important process is termed *reduction*, and is performed in various ways, as will appear by reference to the history of individual metals. The reduction of an oxide is also frequently effected by passing a current of dry hydrogen over it in a heated tube; in this case the oxygen is carried off in the form of water. Sometimes the reduction of an oxide is effected by the aid of another

metal possessed of a very superior attraction for oxygen, as in the cases cited in the preceding paragraph; and in some cases complicated attractions are directed to the process of reduction, as in the production of potassium by the action of red-hot iron upon hydrate of potassa.

Electricity is an all-powerful agent in metallic reduction, and capable, under certain circumstances, of overcoming the most energetic attractions. This important subject has been discussed and illustrated in a former chapter (p. 307).

Some of the metallic combinations, especially those of gold, are reducible by the agency of *light* (p. 200); the salts of silver are also discoloured or partially reduced by the same agency.

The oxidizement of a metal is an essential preliminary to the formation of its oxy-salts, or, in other words, to its combinations with oxy-acids; and in this respect common chemical nomenclature is inaccurate. Thus we speak of sulphate of *copper*, nitrate of *zinc*, &c., meaning sulphate of *oxide* of copper, nitrate of *oxide* of zinc, &c. This ambiguity is prevented with respect to the alkalis and alkaline earths, the oxides of their bases being characterized by a distinct termination: thus phosphate of *soda* means phosphate of *oxide of sodium*, &c.; a circumstance which induced Sir H. Davy to propose an analogous termination for all the oxides, appropriately applied to their common Latin names: *Cupra*, oxide of copper; *Argentæ*, oxide of silver, &c.; but this proposal, which he extended to other compounds, was never adopted.

Each metal has a certain definite quantity of oxygen with which it combines; and where the same metal unites in more than one proportion with oxygen, in the second, third, and other compounds, it is a multiple of that in the first, consistent with the law of definite proportionals. Thus, 100 parts of mercury combine with 4 of oxygen to produce the black oxide, and with 8 to produce the red oxide. Copper also forms two oxides; in the one 12.5 of oxygen are united to 100 of metal, and in the other 25. Where two oxides only are thus formed, that with the minimum of oxygen is termed the *protoxide*, and that with the maximum of oxygen the *peroxide*; where there are three or four distinct steps of oxidizement, the terms *deutoxide* or *binoxide*, and *tritoxide* or *teroxide*, may be applied to the second and third stages; and where the proportion of oxygen, in three oxides, is in the relation of 1, $1\frac{1}{2}$, and 2, the second is termed a *sesquioxide*.

M. F. de Montizon has attempted to show (*Ann. de Ch. et Ph.*, vii. 7) that a relation subsists between the quantity of oxygen with which the metals combine, and their specific gravities; the oxygen being a multiple or submultiple of the density; and he has given a table comparing the results deduced from such a theory, with those obtained by analysis.

In reference to an hypothesis originally propounded by Davy (*Elem. of Chem.*), respecting the possible existence of hydrogen in the metals, and of water in their oxides, Gay Lussac has observed that the lightest metals are those which absorb most oxygen in becoming oxides; and that the heavier or denser metals, on the contrary, absorb less oxygen; in other words, the denser metals are those which have the higher equivalents, the lighter metals being represented by lower numbers: this law, though not rigorously exact, is sufficiently so to deserve attention, and if, selecting

certain metals they be divided into two groups, it will be found that where the specific gravity varies from 10 to 20, the atomic weight is about or above 100, but that where the specific gravity is between 8 and 1, or below 1, the atomic weight is about 30.

I.			II.		
Metal.	Sp. Gr.	Atomic Weight.	Metal.	Sp. Gr.	Atomic Weight.
Platinum	20.98	99	Cobalt	8.53	30
Gold	19.20	200	Copper	8.89	32
Iridium	18.60	96	Nickel	8.27	28
Tungsten	17.50	100	Iron	7.78	28
Mercury	13.56	200	Zinc	7.00	32
Lead	11.35	104	Manganese	6.85	28
Silver	10.47	108	Sodium	0.97	24

Among the combinations of metals with oxygen, some are insoluble in water, or nearly so, and have neither taste nor smell; others are soluble and sour, constituting the *metallic acids*; others are soluble and alkaline, forming the *fixed alkalis* and *alkaline earths*. They are of all colours, and frequently the same metal united to different proportions of oxygen produces compounds differing in colour: thus we have the *black* and *red* oxide of mercury, the *green* and the *black* oxide of manganese, &c.

The different oxides of the same metal frequently form distinct salts with the acids, and the quantity of acid required to neutralize the oxide bears a direct proportion to the oxygen which it contains. Thus, 208 parts of protoxide of mercury, containing 8 of oxygen, combine with 40 of sulphuric acid to form the *protosulphate of mercury*; and 216 parts of the peroxide of mercury, containing 16 of oxygen, require 80 of sulphuric acid to constitute the *persulphate of mercury*. This law was first developed by Gay Lussac (*Mémoires d'Arcueil*, ii. 159). It sometimes happens that the same oxide unites with an acid in two proportions, forming two distinct salts, in which case the acid in the second is a multiple of that in the first. Thus, 48 parts of potassa unite to 22 and to 44 of carbonic acid, forming a *carbonate* and a *bicarbonate* of potassa. We thus have an *oxalate*, a *binoxalate*, and a *quadroxalate*, of potassa, &c.

The metallic oxides occasionally combine with each other, forming definite compounds; instances of such combinations are common in the mineral kingdom: in this case one of the oxides appears to perform the part of an acid, and the other that of base. Many of the compounds of silica furnish illustrative instances. The salts of the proper metallic acids are also analogous compounds.

ACTION OF CHLORINE.—All the metals appear susceptible of combining with chlorine, and of producing a class of compounds which may be termed *metallic chlorides*. There are a few of the metals which resist the action of chlorine at common temperatures, but when heated they all combine with it; some slowly; others rapidly, and with intense ignition. Copper-leaf, powdered antimony, arsenic, &c., burn when thrown into the gas: mercury and iron inflame when gently heated in it; silver, gold, and platinum, quietly absorb it. In these cases, minute mechanical division remarkably accelerates the action. The attraction of chlorine for metals is greater than that of oxygen; consequently when a metallic oxide is heated in chlorine, oxygen is evolved, and a chloride formed.

The insoluble chlorides are also formed by adding solution of chlorine, or of the soluble chlorides, or of hydrochloric acid, to the soluble metallic salts. Thus chloride of silver, which is insoluble, is thrown down from the soluble nitrate of silver by solution of chlorine, of hydrochloric acid, and of common salt: hence, too, all the soluble chlorides are recognised, by yielding a white precipitate with solution of nitrate of silver, which is soluble in ammonia, and which, when pure, rapidly blackens by exposure to the sun's rays.

The physical and chemical properties of the chlorides are extremely various. They are nearly of all colours. They are generally unchanged by heat; but some undergo decomposition. Some are soluble, others insoluble, in water. Some permanent; others deliquescent. Several of them decompose water, and form hydrochloric acid, and an oxide. The question respecting the action of water upon the chlorides has given rise to several hypotheses founded on their mutual decomposition, some of which will be adverted to under specific heads. (See DUMAS, in reference to this question. *Ann. de Ch. et Ph.*, xlv. p. 263.) Many of them absorb ammonia, and some in considerable quantity. They are fusible, and most of them crystallizable. Some are extremely volatile at common temperatures, and others fixed in high heats. A few exist, at all ordinary temperatures, in the liquid state. They are generally decomposed by a red heat by hydrogen, which produces hydrochloric acid, and reduces the metal. Anhydrous sulphuric acid appears not to act upon them; but the common hydrated acid decomposes them, with few exceptions, evolving hydrochloric acid: the theory of these changes is elsewhere explained. (See *Chloride of Sodium*.) Some of the metals rapidly decompose certain chlorides in consequence of their superior attraction: thus chloride of silver is decomposed by zinc, &c.

The same metal often forms more than one compound with chlorine, and these compounds are designated as the oxides. Thus we have the *protochloride* and *bichloride* or *perchloride* of mercury, *sesquichloride* of antimony, &c.

Many of the metals decompose hydrochloric acid, in which case hydrogen is evolved, and a metallic chloride produced; and when metallic oxides are heated in hydrochloric acid, they generally give rise to the formation of a chloride and water. (See page 399, &c.)

There are a few metallic oxides which, at low temperatures, absorb and retain chlorine, but they hold it by very feeble attraction. The chlorides of potassa and of lime will be described under those bodies. It has also been combined with the oxides of iron, zinc, and copper. (GROUVELLE, *Ann. de Ch. et Ph.*, xvii.) These compounds are decomposed by heat and by the acids.

ACTION OF CHLORIC ACID.—The compounds of the metallic oxides with chloric acid, or *chlorates*, are decomposed by heat with the copious evolution of oxygen, and a chloride generally remains: they deflagrate when triturated with charcoal or other combustibles. In the neutral chlorates the proportion of oxygen in the base to that in the acid is as 1 to 5: some of these salts have been long known, others only recently investigated. The *oxychlorates*, or *perchlorates*, have been scarcely

examined. Like the chlorates, they yield oxygen when heated: and the proportion of oxygen in the base to that in the acid is as 1 : 7.

ACTION OF IODINE.—Iodine, aided by heat, acts upon many of the metals, and produces *metallic iodides*. Some of these are soluble in water without decomposition; others decompose water; others are insoluble. The insoluble iodides may generally be formed by adding a solution of iodine or of hydriodic acid, or of an iodide, to the soluble metallic salts. Iodine often combines in more than one proportion with metals, forming *protiodides*, *sesquiodides*, *biniodides*, &c. The iodides are decomposed by chlorine and bromine, and some by oxygen; but in other instances iodine expels oxygen from its combinations with the metals. Iodides are also decomposed by nitric and by sulphuric acid; and in all these cases the free iodine is easily recognised by starch. According to Gay Lussac, when the vapour of iodine is passed over hot lime, baryta, and strontia, it does not expel their oxygen, but unites with them as oxides. These compounds are not very permanent, and are decomposed at a temperature a little exceeding that required to form them.

ACTION OF IODIC ACID.—The compounds of this acid with the metallic oxides have been but little examined: they are decomposed and converted into iodides by heat, sometimes with the evolution of oxygen only; at others, iodine is also given off.

ACTION OF BROMINE.—Bromine combines with the metals and produces *bromides*, analogous in their general habitudes to the chlorides and iodides; they are formed either by the direct action of bromine on the metal, or by that of hydrobromic acid upon the metallic oxide; or, when insoluble, they are precipitated by the addition of the soluble bromides to metallic solutions. Bromine also unites to some of the metallic oxides, and produces bleaching compounds. Chlorine disengages bromine from its binary metallic compounds, and bromine expels iodine from the iodides; so that the attraction of bromine for the metals is intermediate between chlorine and iodine. (See a Memoir on the Bromates by M. BERTHEMOT, *Ann. de Ch. et Ph.*, xlv. 382.)

The *Bromates* are little known. When heated to redness they become *bromides*, by the loss of oxygen.

ACTION OF FLUORINE.—As fluorine has not been obtained in a separate state, its immediate action upon the metals is not known; but it would probably be energetic. Such of the *fluorides* as are insoluble may be obtained by the medium of a solution of fluoride of potassium, or by precipitation by hydrofluoric acid: the soluble fluorides are formed by digesting the oxides in the hydrofluoric acid. The fluorides are not decomposed by oxygen, chlorine, iodine, or bromine; but they are immediately recognised by the evolution of hydrofluoric acid, when moistened and heated with sulphuric acid, and by their action upon glass under such circumstances.

ACTION OF HYDROGEN.—Hydrogen forms permanent compounds with two of the metals only, namely, arsenic and tellurium. It appears to combine with each in two proportions, forming two solid compounds, the *hydrurets* or *hydrogurets* of arsenic and tellurium; and two gaseous

compounds, *arseniuretted* and *telluretted hydrogen*. At high temperatures it dissolves potassium, forming *potassiuretted hydrogen gas*. Hydrogen also appears to combine with zinc and antimony, at least it frequently retains a little of those metals in its gaseous state.

There are many of the metallic oxides and chlorides, which are decomposed by hydrogen: the oxides are reduced with the formation of water, and the chlorides with the production of hydrochloric acid.

ACTION OF WATER.—Those metals which are speedily acted upon by common air and oxygen, are also generally capable of decomposing water; some of them rapidly, others slowly. There are some metals which are not acted upon by air deprived of moisture, nor by water deprived of air; but moist air, or water containing air, effects their oxidizement: this appears to be the case with iron, (Dr. MARSHALL HALL, *Quarterly Journal*, vii. 55,) and also with lead. Water combines with many of the metallic oxides, and produces *hydrated oxides*, or *metallic hydrates*. In these the relative proportion of water is definite. Some are easily decomposed by very moderate heat, as hydrate of copper; others retain water even when heated to redness, as hydrate of potassa; others are decomposed at a red heat, as hydrate of lime.

ACTION OF NITRIC ACID.—The greater number of metals are capable of decomposing nitric acid by the abstraction of a part of its oxygen, and thus of resolving it into some of the other nitric compounds; nitric acid is a very generally acting solvent, therefore, of these bodies. It dissolves nearly all the metallic oxides, and produces a numerous class of *nitrates*, which, if prepared with heat and with excess of acid, generally contain the metal at its maximum of oxidizement. The nitrates are all decomposed by a red-heat; they give off oxygen and nitrogen, either separate or combined, and the metallic oxide remains. They are also decomposed when heated with sulphur, phosphorus, or charcoal; and sulphurous, phosphoric, and carbonic acids are formed: the phosphoric, being a fixed acid, remains united to the metallic oxide; while the sulphurous and carbonic acids are usually expelled. The nitrates are decomposed by sulphuric acid, nitric acid is evolved, and *sulphates* are formed. In the neutral nitrates the proportion of oxygen in the acid is to that in the base as 5 to 1. Thus in the nitrate of potassa, 48 parts of potassa, containing 8 of oxygen, are combined with 54 of nitric acid, containing 40 (8×5) of oxygen; and in the nitrate of oxide of copper, 40 parts of oxide of copper, containing 8 of oxygen, are combined with 54 of nitric acid, containing 40 of oxygen.

ACTION OF AMMONIA.—At high temperatures some of the metals are capable of decomposing ammonia. Liquid ammonia dissolves several of the metallic oxides, and with some of them forms crystallizable compounds. It dissolves the oxides of silver, copper, zinc, arsenic, antimony, and tellurium; the protoxides of iron, cobalt, and nickel; and the peroxides of tin, mercury, gold, and platinum. These compounds are all decomposed by heat. The compounds of ammonia with the oxides of gold, silver, and platinum, detonate when heated, and the oxide and the ammonia are both decomposed. The combinations of ammonia with several anhydrous salts have been examined by H. Rose (*Ann. de Ch. et Ph.*, lxii. 308).

ACTION OF SULPHUR.—All the metals appear capable of combining with sulphur and forming *sulphurets*. These are obtained, 1st, By heating the metal in a close vessel, with sulphur; and it not unfrequently happens that, during the combination, the metal becomes intensely ignited, burning as it were in the vapour of the sulphur, and furnishing a striking instance of combustion without the presence of oxygen; this is the case with potassium and sodium, and with the filings or shavings of copper, lead, and iron. 2ndly, By heating a mixture of sulphur and a metallic oxide, in which case sulphurous acid escapes, and the metallic sulphuret remains behind. 3rdly, By decomposing the *sulphates*, either by subjecting them to the action of a current of hydrogen gas in a heated tube, or by heating a mixture of the sulphate with charcoal. 4thly, By the action of sulphuretted hydrogen. 5thly, By fusing the metallic oxide with a mixture of carbonate of potassa and sulphur, in which case an alkaline sulphuret is first formed, and sustains a red heat, but at that temperature a proportion of its sulphur is imparted to the reduced metal of the oxide. The sulphurets are in general brittle; some have a metallic lustre, and are opaque; others are without lustre, and more or less transparent. Some are fusible, and some volatile. Some are soluble, but the greater number insoluble in water. Where the same metal forms two sulphurets, the sulphur in those containing the largest proportion is a simple multiple of the sulphur in those containing the smallest proportion; hence we have metallic *sulphurets*, *bisulphurets*, and *sesquisulphurets*; and, generally speaking, the sulphurets correspond in number and atomic composition with the oxides. When the metallic sulphurets are heated in close vessels, some undergo no change, as those of sodium and potassium; others sublime unaltered, as sulphuret of mercury and sulphuret of arsenic; others lose a portion of their sulphur, and, if air be admitted, sulphurous acid escapes, and the metal passes into the state of oxide, as sulphuret of lead and sulphuret of copper; and it is thus that these sulphurets are oxidized by the process called *roasting*, previous to their reduction, upon the large scale; others again are entirely decomposed, the metal being completely reduced; this happens on heating sulphuret of platinum or of gold. Definite compounds of sulphur with some of the metallic oxides, have been obtained by Arfwedson (*Ann. de Ch. et Ph.*, vi. 204).

There are certain double sulphurets, which Berzelius has designated *sulphur salts*; in these cases he terms the electronegative sulphurets, *sulphur acids*; and the electropositive sulphurets, *sulphur bases*; among the *sulphur acids*, he enumerates the sulphurets of arsenic, antimony, gold, molybdenum, tellurium, tin, and tungsten; he also calls sulphuretted hydrogen, sulphocyanogen, sulphuret of selenium, and sulphuret of carbon, *sulphur acids*. The principal *sulphur bases* are the proto-sulphurets of the metals of the alkalis and alkaline earths, and the hydro-sulphuret of ammonia (sulphuret of ammonium).

HYPOSULPHUROUS ACID combines with the metallic oxides, and produces a class of salts termed *hyposulphites*. Several of these have been examined by Herschel. (*Edin. Phil. Journal*, i.) In some of their characters they resemble the sulphites: they are easily soluble; of a bitter or

sweet taste ; and decomposed by a heat below redness, and by almost all other acids. Their solutions readily dissolve chloride of silver.

SULPHUROUS ACID combines with many of the metallic oxides, producing *sulphites*; in some instances oxygen is transferred from the oxide to the acid, and sulphates result.

The *sulphites* are soluble in water, and have a sulphurous taste and smell. Exposed to moist air, they absorb oxygen, and pass into the state of sulphates. They are decomposed by sulphuric acid, which expels sulphurous acid, and the salts are converted into sulphates. When perfectly pure they are not affected by solution of baryta.

HYPOSULPHURIC ACID forms with the metallic oxides a class of *hyposulphates*. They do not afford precipitates with solution of baryta. When heated they evolve sulphurous acid, and are converted into neutral sulphates: when their solutions are boiled with sulphuric acid, sulphurous acid is evolved, but no sulphur is precipitated.

SULPHURIC ACID, in its concentrated state, and unaided by heat, is acted upon by a few of the metals only; when diluted, some of them are oxidized at the expense of the water, hydrogen is evolved, and the metallic oxide combines with the acid, producing a *sulphate*. In these cases the hydrogen evolved is the indicator of the quantity of oxygen transferred to the metal; every volume of hydrogen is the equivalent of half a volume of oxygen, and accordingly the production of 100 cubic inches of hydrogen indicates the transfer of 50 of oxygen, or, by weight, of about 17.3 grains. As different metals unite to different weights of oxygen, they will obviously evolve different quantities of hydrogen. Thus, if one metal, to become soluble in sulphuric acid, require to be united with 10, and another with 20 per cent. of oxygen, the latter will evolve twice the volume of hydrogen, compared with the former. As the evolution of hydrogen, during the solution of a metal in dilute sulphuric acid, is referable to its oxidizement, no hydrogen will be evolved by the action of the acid upon an oxide, but it will be merely dissolved.

The sulphates are an important class of salts. The greater number of them are soluble in water, and the solutions yield a precipitate with the soluble salts of baryta which is insoluble in acids and alkalis. The insoluble sulphates may be recognised by igniting them in fine powder with thrice their weight of carbonate of soda, by which a soluble sulphate of soda is formed: it may be separated by water and filtration, crystallized, and tested by nitrate of baryta. The sulphates of potassa, soda, lithia, lime, baryta, and strontia, resist a white heat without decomposition: the other sulphates evolve, when intensely heated, sulphuric acid, sulphurous acid, and oxygen. Many of them are decomposed at high temperatures by the action of hydrogen, which carries off the oxygen of the acid, and of the base, and leaves a metallic sulphuret. In some cases the sulphur also combines with the hydrogen, and the sulphate thus affords a reduced metal. They are all decomposed at a red heat by charcoal, and most of them are thus converted into sulphurets; carbonic acid, and carbonic oxide, being at the same time evolved. In the neutral sulphates the proportion of oxygen in the acid is to that in the base as 3 to 1. Thus sulphate of soda is composed of 32 soda, containing 8 of oxygen, combined with 40 of sulphuric acid, containing 24 (8×3) of oxygen; and in the sulphate of copper, 40

parts of oxide of copper, containing 8 of oxygen, are combined with 40 of sulphuric acid, containing 24 (8×3) of oxygen. Many of the anhydrous sulphates absorb ammoniacal gas, forming definite compounds which are decomposed by heat. (H. ROSE, *Ann. de Ch. et Ph.*, Lxii. 309.)

ACTION OF SULPHURETTED HYDROGEN.—When sulphuretted hydrogen combines with metallic sulphurets, it forms one class of the *sulphur-salts*. It seems doubtful whether any of the metals combine with sulphuretted hydrogen. Its combinations with their oxides have been termed *hydrosulphates* or *hydrosulphuretted oxides*, but it generally happens that in the mutual action of the sulphuretted hydrogen and the oxide, both are decomposed, the hydrogen combining with the oxygen of the oxide to form water, and the sulphur uniting to the metal to form a metallic sulphuret. In a few cases the metallic oxide is reduced. Occasionally a compound of a metallic sulphuret and a salt of the oxide is thrown down; thus when sulphuretted hydrogen is passed through a solution of per-nitrate of mercury, the latter being in excess, the precipitate is a definite compound of pernitrate and sulphuret of mercury. (H. ROSE, *Ann. de Ch. et Ph.*, Lxvi. 366.) The following table shows the effect of sulphuretted hydrogen and of sulphuretted hydrosulphuret of ammonia upon solutions of several of the metals, as far as *colour* of the precipitate is concerned, these precipitates being often resorted to as qualitative tests.

METAL.	SOLUTION.	SULPHURETTED HYDROGEN.	HYDROSULPHURET OF AMMONIA.
MANGANESE .	Neutral protochloride	No precipitate	Copious ochre-yellow
IRON . . .	Neutral protosulphate	Blackish and small in quantity	Black and abundant
Ditto . . .	Perchloride	Abundant black	Black
ZINC . . .	Chloride	A little opalescent and then milky	Straw-colour and copious
TIN	Acid protochloride	Brown	Deep orange
Ditto . . .	Acid perchloride	At first 0, then yellow and copious	Apple-green
CADMIUM . .	Chloride	Yellow	Yellow
COPPER . . .	Protochloride	Deep brown	Brown
Ditto . . .	Nitrate	Black	Brown and black
LEAD	Chloride and nitrate	Ditto	Ditto
ANTIMONY . .	Tartrate of antimony and potassa	Deep orange-red	Bright orange
BISMUTH . .	Tartrate of bismuth and potassa	Deep brown	Deep brown
COBALT . . .	Chloride	0 but blackish	Copious black
URANIUM . .	Sulphate	Brown	Blackish brown
TITANIUM . .	Acid chloride	0	Black
Ditto . . .	Neutral sulphate	0	Green
CERIUM . . .	Protosalts	0	White
TELLURIUM .	Sulphate	Black	Black
ARSENIC . . .	White oxide	Yellow	Yellow
Ditto	Arsenic acid	Ditto	Ditto
NICKEL . . .	Sulphate	Brown	Black
MERCURY . .	Acid nitrate	Black, then gray, and black by excess of test	Black by excess of test
Ditto	Acid pernitrate	Ditto	Ditto
Ditto	Corrosive sublimate	Brown by excess of test	Ditto
OSMIUM . . .	Solution of oxide	Metallic	Metallic
PALLADIUM .	Chloride	Brown	Brown
SILVER . . .	Nitrate	Black and metallic	Ditto
GOLD	Chloride	Black and reduced gold	Yellow
PLATINUM . .	Ditto	Deep brown	Pale brown

ACTION OF SELENIUM.—Selenium acts upon the metals with nearly the same phenomena as sulphur, and in their general characters the *seleniurets* and sulphurets are analogous: when heated in the open fire the selenium burns slowly off with an azure flame, and the odour of radish. The atomic composition of the seleniurets follows that of the sulphurets, and they are best obtained by precipitating the metallic solutions with seleniuretted hydrogen, and then, if biseleniurets are required, the precipitate may be fused with selenium, and the excess driven off by distillation. The *selenites* and *seleniates* are decomposed by sulphurous acid, which throws down the selenium of a red colour in the cold, and nearly black at a boiling-heat. Distilled with hydrochlorate of ammonia, selenium passes over. In the selenites the oxygen in the acid is to that in the base as 2 to 1, and in the seleniates as 3 to 1; these salts, therefore, are isomorphous with the sulphites and sulphates.

ACTION OF PHOSPHORUS.—Phosphorus combines with the greater number of the metals, forming a series of *metallic phosphurets*. There are three methods of forming them; either by heating a mixture of phosphorus and the metal, or projecting phosphorus upon the metal previously heated to redness; or by heating a mixture of the metal or its oxide, with phosphoric acid and charcoal; or by passing phosphuretted hydrogen over the heated metallic oxide. A very few only of the phosphurets can be obtained in the humid way, for when phosphuretted hydrogen is passed through metallic solutions the metal is either reduced, as in the case of the salts of gold and silver; or peculiar compounds ensue, composed of the metallic salt and the phosphuret, as when the salts of peroxide of mercury are decomposed by phosphuretted hydrogen; or no change takes place, as with the greater number of metallic salts. The only case of the production of a pure phosphuret by this process appears to be that of phosphuret of copper, which is thrown down whenever phosphuretted hydrogen is passed through solutions of the salts of that metal. (H. ROSE, *POGGEND. Ann.*, xxiv. 320; and *Ann. de Ch. et Ph.*, lxvi. 366.) The phosphurets have a metallic lustre; if they contain a difficultly-fusible metal, they are more fusible than the metal they contain; if an easily-fusible metal, less so. They are mostly crystallizable, and totally or partly decomposable at a high temperature. The greater number of the phosphurets have only been examined by Pelletier (*Ann. de Ch.*, tom. i. and xiii., and *Mémoires et Observations de Chimie*). The existence of compounds of metallic oxides with phosphorus appears doubtful.

When phosphorus is introduced into the solutions of those metals which have but a feeble attraction for oxygen, it reduces them to the metallic state. Thus gold, silver, and platinum are thrown down by immersing a stick of phosphorus into their respective solutions.

The *Hypophosphites* and the *Phosphites* have been imperfectly examined. When heated they evolve phosphorus or phosphuretted hydrogen, and are converted into phosphates: their solutions smell of phosphorus, and reduce the salts of gold, silver, and mercury.

ACTION OF PHOSPHORIC ACID.—The *metallic phosphates* may be formed either by dissolving the oxides in phosphoric acid, or by adding a solution of phosphoric acid, or of an alkaline phosphate, to solutions of

those metals which form insoluble or difficultly-soluble phosphates. The greater number of the phosphates are decomposed and converted into phosphurets, by ignition with charcoal: and those containing volatile oxides are volatilized at high temperatures. The phosphates of ammonia, potassa, and soda, are soluble; but the greater number of these salts are difficultly soluble, and some insoluble in water: they are dissolved by phosphoric, nitric, and hydrochloric acids, and precipitated, generally without change, by ammonia. Those which are insoluble are mostly decomposed by boiling with carbonate of potassa. Several of the phosphates occur in the native state, constituting some beautiful but generally rare minerals.

In the neutral phosphates the quantity of oxygen in the acid is to that in the base as 2·5 to 1. Thus, phosphate of soda consists of 32 soda containing 8 oxygen, and 36 phosphoric acid containing 20 ($8 \times 2\cdot5$) of oxygen. But the phosphoric acid unites to bases in several other proportions, giving rise to a variety of subsalts and supersalts, of which the most important will be noticed in the sequel.

ACTION OF CARBON.—Carbon unites to very few of the metals; and of the metallic *carburets*, one only is of importance, namely, carburet of iron, which constitutes the varieties of cast-iron, and steel.

When some of the metallic cyanurets, and certain of the salts of metallic oxides and organic acids are decomposed by heat, the residuary products appear to be, in some cases, true carburets; these, however, have been but imperfectly examined.

CARBONIC ACID unites with the greater number of the metallic oxides, and forms *carbonates*, of which the distinctive characters have already been noticed; most of them are of difficult solubility, and may be formed by adding an alkaline carbonate to the metallic solution. Of the carbonates some are entirely, and others only partially, decomposed at a red heat. Carbonate of magnesia, for instance, loses the whole of its carbonic acid at a red heat; carbonate of potassa retains it; and bicarbonate of potassa loses one-half, and passes into the state of carbonate. The carbonates are decomposed by nearly all the other acids, and are then distinguished by the effervescence that ensues on the escape of carbonic acid gas.

In the neutral carbonates the proportion of oxygen in the base is to that in the acid as 1 to 2. Carbonate of potassa, for instance, consists of 48 of potassa containing 8 of oxygen, and 22 of carbonic acid, containing 16 (8×2) of oxygen.

The carbonates are not uncommon natural products.

CYANOGEN combines with many of the metals, and forms compounds, which we call *cyanurets*, or *cyanides*. The compounds of the *cyanic acid*, or the *cyanates*, are so decomposed, either by the action of water, or the acids, that the cyanic acid is resolved into carbonic acid and ammonia, with no trace of hydrocyanic acid. The *fulminates* explode when heated, and evolve hydrocyanic acid by the action of the oxyacids. The *Hydrocyanates* have been but imperfectly examined; they appear peculiarly susceptible of decomposition.

Sulphocyanurets and *Sulphocyanates* produce a characteristic red colour when added to a solution of persulphate of iron.

THE ACTION OF BORON upon the metals has not been fully investigated.

THE BORATES of the alkalis are soluble: with other bases the boracic acid mostly forms difficultly-soluble or insoluble compounds, which are easily formed by adding solution of boracic acid, or a soluble borate to the metallic solution. The borates are generally decomposed in the humid way, by sulphuric, nitric, and hydrochloric acids; but, at a red heat, the boracic acid expels the more volatile acids from their basic compounds. The presence of this acid may in many instances be detected by digesting its compounds in sulphuric acid, evaporating to dryness, and boiling the residue in alcohol, which will then be found to burn with a characteristic green flame. (See *Boracic Acid*.)

ACTION OF THE METALS UPON EACH OTHER.—The metals may, for the most part, be combined with each other, forming a very important class of compounds, the *metallic alloys*. In the act of combination they generally evolve heat; thus, when platinum and tin-foil are fused together, there is vivid ignition; so, also, when melted zinc and copper are suddenly mixed in the proportions to form brass, the increase of heat is such as to vaporize part of the metal. Various processes are adopted in the formation of alloys, depending upon the nature of the metals. Many are prepared by simply fusing the two metals in a covered crucible; but if there be a considerable difference in the specific gravity of the metals, the heavier will often subside, and the lower part of the bar or ingot will differ in composition from the upper; this may be to a great extent prevented by agitating the alloy till it solidifies. Mr. Hatchett found that when an alloy of gold and copper was cast into bars, the moulds being placed perpendicularly, the upper part of the bar contained more copper than the lower (*Phil. Trans.*, 1803); and although copper and silver appear readily to combine, it is extremely difficult to form a bar of their alloy, of perfectly uniform composition throughout.

Where one of the metals is very volatile, it should generally be added to the other after its fusion; and if both metals be volatile, they may be sometimes united by distilling them together.

It has been a question whether alloys are to be considered as compounds, or as mere mixtures; but, in many cases, their properties leave little doubt of their being real compounds, and in some cases they are found to unite in definite proportions only; and it is not improbable that all the alloys contain definite compounds of the metals. It is observed by Berzelius, that the acidifiable metals have the greatest tendency to combine with those which produce salifiable bases, and that arsenic, antimony, and tellurium, form definite compounds analogous to sulphurets and phosphurets, which are not uncommon as ores. Among the artificial, as well as the natural alloys, there are many which are crystallizable, and the true compound may sometimes be separated from the mere mixture of the metal by its tendency to crystallize.

The principal characters of the alloys are the following:—i. We observe a change in the ductility, malleability, hardness, and colour. Malleability and ductility are usually impaired, and often in a remarkable degree: thus gold and lead, and gold and tin, form a brittle alloy. The alloy of copper and gold is harder than either of its component parts; and a minute quantity of arsenic added to copper renders it white.—ii. The specific gravity of an alloy is rarely the mean of its component parts, in some cases an increase, in others a diminution of density having taken place, as shown in the following table from Thenard (*Traité de Chimie*, vol. i., p. 394):—

Alloys possessed of greater specific gravity than the mean of their components.

Gold and Zinc
" Tin
" Bismuth
" Antimony
" Cobalt
Silver and Zinc
" Lead
" Tin
" Bismuth
" Antimony
Copper and Zinc
" Tin
" Palladium
" Bismuth
" Antimony
Lead and Bismuth
" Antimony
Platinum and Molybdenum
Palladium and Bismuth.

Alloys having a specific gravity inferior to the mean of their components.

Gold and Silver
" Iron
" Lead
" Copper
" Iridium
" Nickel
Silver and Copper
Copper and Lead
Iron and Bismuth
" Antimony
" Lead
Tin and Lead
" Palladium
" Antimony
Nickel and Arsenic
Zinc and Antimony.

iii. The fusibility of an alloy is generally greater than that of its components. Thus platinum, which is infusible in our common furnaces, forms, when combined with arsenic, a very fusible alloy; and an alloy of certain proportions of lead, tin, and bismuth, is fusible at 212° , a temperature many degrees below the melting-point of its most fusible constituent.

iv. Alloys are generally more oxidizable than their constituents, taken singly; a property which is, perhaps, partly referable to the formation of an electrical combination. Where an alloy consists of two metals, the one easily and the other difficultly oxidizable, it may be decomposed by exposing it to the action of heat and air, the former metal being converted into an oxide: its last proportions, however, are often not easily separated, being protected by combination with the least oxidizable metal. An alloy of three parts of lead and one of tin is infinitely more oxidizable than either of its components, and easily burns at a dull-red heat.

v. The action of acids on alloys may generally be anticipated by a knowledge of their effects upon the constituent metals; but if a soluble metal be alloyed with an insoluble one, the former is often protected by the latter from the action of an acid. Thus, silver alloyed with a large quantity of gold, resists the action of nitric acid in consequence of the

insolubility of the latter metal in that acid; and, in order to render it soluble, it is requisite that it should be made to form about a fourth part of the alloy, in which case the nitric acid extracts it, and leaves the gold in an insoluble film or powder.

In other cases a metal insoluble, or nearly so, in certain acids, *per se*, is taken up in considerable quantity when alloyed; thus, platinum is insoluble in nitric acid, but its alloy with silver is to a certain extent soluble; and when a triple alloy of gold and silver with a little platinum is rolled out and digested in nitric acid, both the silver and the platinum are taken up. Rhodium is insoluble in acids, but, when alloyed with copper or lead, the nitrohydrochloric acid dissolves it.

Various classifications of the metals have been adopted by chemical authors*, some dependent upon their *physical*, others upon their *chemical* properties. The former can scarcely be considered as adapted to chemical inquiry, and the latter involve numerous difficulties in consequence of the gradual transition of metals of one class into those of another. I shall consider the metals in the order in which they are set down in the following table, and which is nearly that of their respective attractions for oxygen, with the exception of the last division, which includes substances in part imperfectly examined, and from which, as already remarked, silicium ought probably to be excluded.

I.	II.	III.	IV.	V.	VI.
1 Potassium	8 Manganese	15 Copper	24 Arsenic	30 Mercury	38 Glucium
2 Sodium	9 Iron	16 Lead	25 Molybdenum	31 Silver	39 Zirconium
3 Lithium	10 Zinc	17 Antimony	26 Chromium	32 Gold	40 Yttrium
4 Calcium	11 Tin	18 Bismuth	27 Vanadium	33 Platinum	41 Thorium
5 Barium	12 Cadmium	19 Uranium	28 Tungsten	34 Palladium	42 Aluminium
6 Strontium	13 Cobalt	20 Titanium	29 Columbium	35 Rhodium	43 Silicium.
7 Magnesium	14 Nickel	21 Cerium		36 Osmium	
		22 Lanthanum		37 Iridium	
		23 Tellurium			

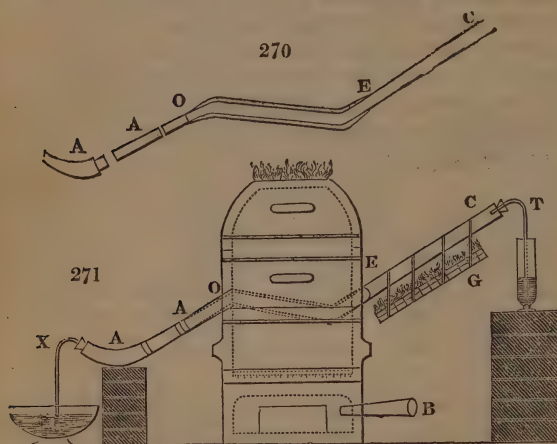
* Berzelius divides the metals into two leading classes: 1. Bases of the alkalis and earths; 2. Bases of the oxides and acids. The former are distinguished by their low specific gravity, being either lighter, or but little heavier than water, and they are so easily oxidized as to decompose water at common temperatures: in this list he includes Kalium (Potassium), Natrium (Sodium), Lithium, Ammonium (the hypothetical base of ammonia), Barium, Strontium, Calcium, Magnium (Magnesium), Aluminium, Beryllium (Glucium), Yttrium, and Zirconium. The second class he subdivides into, 1. Electronegative metals; that is, such as in combination with oxygen have a greater tendency to form acids, than oxides or salifiable bases; these are Selenium? Arsenic, Chromium, Molybdenum, Wolframium (Tungsten), Antimony,

Tellurium, Tantalum (Columbium), Titanium, Osmium, and Gold. 2. Electropositive metals, or such as in combination with oxygen especially produce salifiable bases: these are Platinum, Iridium, Rhodium, Palladium, Silver, Mercury, Uranium, Copper, Bismuth, Tin, Lead, Cadmium, Zinc, Nickel, Cobalt, Iron, Manganese, Cerium. The metals of the two last divisions are all more than four times heavier than water, very few of them are oxidized at common temperatures either by air or water, and their oxides are reduced by charcoal at high temperatures, and by potassium, at a moderate heat. See also Thenard (*Traité de Chimie*), and an essay on the action of the vapour of water, at high temperatures, on the metals and their sulphurets, by M. V. Regnault (*Ann. de Ch. et Ph.*, Lxii. 337).

§ I. POTASSIUM.

POTASSIUM (or Kalium of the German chemists) was discovered in 1807 by Sir Humphry Davy (*Phil. Trans.*, 1808). He obtained it by submitting hydrate of potassa, or caustic potash, to the decomposing action of Voltaic electricity: the metal was slowly evolved at the negative pole. By this process, however, it could only be procured in very minute quantities; and various other methods have been devised. The following is that described by Gay Lussac and Thenard (*Recherches Physico-chymiques*).

A sound and perfectly clean gun-barrel is bent, as shown in the annexed sketch (fig. 270). It is then covered with an infusible lute between the letters o and E, and the interior of the luted part is filled



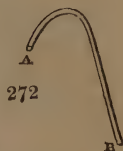
with clean iron-turnings. Pieces of fused potassa are then loosely placed in the barrel between E and C. A A is a copper tube and small receiver, which are adapted to the extremity o, and to each other, by grinding. This apparatus is next transferred to the furnace, arranged as shown in fig. 271, x and t representing two glass

tubes dipping into mercury. The furnace is supplied with air by a good double bellows entering at B, and a small wire basket, G, is suspended below the space E C.

The part of the barrel in the furnace is now cautiously raised to a white heat, and the escape of air by the tube x shows that all is tight. Some burning charcoal is then put at the end E, of the cage G, which causes a portion of potassa to liquify and fall into the lower part of the barrel upon the iron. Hydrogen gas instantly escapes by the tube x, and attention must now be had to keep the copper tubes A A cool, by laying wet cloths upon them. When the evolution of gas ceases, fresh charcoal is placed under the potassa, and so on till the whole has passed down; if too much potassa be suffered to fall at once, the extrication of gas at x will be very violent, which should be avoided. If the space between A and o should become stopped by potassium, gas will issue by the tube t (which must always be under a greater pressure of mercury than the tube x), and the potassium must be cautiously fused by applying hot charcoal to the copper tube, when the gas will again appear at x and cease at t. When the operation is concluded, the tubes x and t are

removed, and corks quickly applied to the holes; and when the apparatus is cool, the barrel is carefully removed from the furnace, and a little naphtha suffered to run through it. The potassium is found in globules in the tube and receiver A A, and considerable portions often lodge at o. The success of this operation is certain, if the heat has been sufficient: but the barrel, if not very carefully covered with lute, is apt to melt, and much, if not the whole, of the product is lost.

Besides the above, there are other methods of obtaining potassium. M. Brunner (*Quarterly Journal*, xv. 379) employs a spheroidal wrought-iron bottle, of a capacity between a pint and a quart, and a piece of gun-barrel of the annexed shape is fitted to its neck by grinding at the end A. When this bottle is charged and well luted it is placed in a proper furnace, nearly perpendicularly, and so that the greater part of the tube may be exposed to heat (it being protected by coils of iron-wire rolled round it), while the end B projects, and has attached to it a copper receiver with a small safety-tube. This receiver, when in use, is about half filled with naphtha, and kept cold by ice or cold water. The bottle is charged with four ounces of fused caustic potassa, introduced, in small portions, alternately, with 6 ounces of clean iron-turnings broken in a mortar, and 1 ounce of powdered charcoal; and this mixture is covered by 2 ounces more of iron-turnings: it is then placed in a furnace, and a glass tube inserted into the protruding barrel at B. As soon as the whole acquires a bright red-heat, inflammable gas is evolved, which burns with a violet flame, and shortly after the green vapour of potassium is seen in the glass tube, which is then removed, and the copper receiver substituted, so that the end B may dip into the naphtha. When the evolution of gas ceases, the fire is extinguished, and the receiver carefully removed. A very successful result furnished 150 grains of potassium, in small globular masses. In another experiment the mixture in the retort consisted of 8 ounces of pure and fused carbonate of potassa, 6 of iron-turnings, finely bruised, and 2 of charcoal: from these, 140 grains of potassium were obtained. Calcined tartar was also sometimes employed instead of other forms of potassa.



The theory of these operations is by no means clearly understood in its minute details. When pure hydrate of potassa is employed in the gun-barrel experiment, more than a fourth of its weight of potassium is never obtained; the remainder is chiefly found partly undecomposed and partly in combination with the produced oxide of iron, forming a hard brittle compound, difficultly acted on by water. The evolution of potassium is evidently dependent upon the attraction of the iron at a high heat for oxygen; the water of the potassa is at the same time decomposed, and possibly the nascent hydrogen may perform its part in the reduction: the readiness with which potassium assumes the elastic state at high temperatures also contributes to its evolution; yet, when the exceedingly powerful attraction of potassium for oxygen is considered, the process is, as to its theory, obscure.

Obtained by the aid of charcoal, potassium generally contains a little carbon, which may be separated by redistilling it in a small iron or even

glass retort, with its beak dipped into naphtha, but this is a troublesome process, and generally attended by some loss of the metal.

Wöhler has described a modification of the potassium apparatus, and a peculiar receiver for its condensation, contrived by Berzelius, of which a description will be found in the twenty-second volume of the *Quarterly Journal*, p. 206. He employs carbonate of potassa produced by calcining tartar, and uses charcoal as the reducing agent. In all these arrangements it is a point of importance to have the tubes, through which the metal passes into the naphtha, as short as possible, and of a sufficient diameter, otherwise they are apt to become plugged up*. The process for obtaining potassium usually followed in Germany is described by Mitscherlich, (*Elements of Chemistry*,) and also by Graham: a mixture of calcined tartar and coarsely powdered charcoal is employed, which is heated in an iron bottle.

Potassium is a blueish-white metal of great lustre. It instantly tarnishes by exposure to air, and is gradually converted into an oxide. At 60° it is malleable, and of the consistency of wax. Its specific gravity is about 0.865. It is most conveniently preserved in naphtha, either by immersing it in that liquid, or by dipping the pieces of metal into it, and keeping them thus varnished, in a small well-stopped phial. When used, the exterior must be wiped with blotting-paper, or scraped; or the naphtha may be driven off by a gentle heat. At 150° it enters into perfect fusion; and at a bright red heat, in close vessels, it boils, and rises in green vapour. At 32° it is a hard and brittle solid, of a crystallized texture. If heated in air, it burns with a brilliant purple flame. It is an excellent conductor of electricity and of heat, and its lustre is well shown by fusing it under naphtha upon a piece of crown-glass, to which it will adhere, and through which it is seen as brilliant as mercury.

POTASSIUM AND OXYGEN. PROTOXIDE OF POTASSIUM. POTASSA. ($po + o$) or P. (Potassium is represented by the German chemists by the symbol K, from *kalium*, the name by which they have chosen to designate the metal, instead of adopting the term potassium applied to it by its discoverer. Potassa they represent by KO or K.)

* During the distillation of potassium from a mixture of carbonate of potassa and charcoal, a gray compound distils over, which, by the action of water, yields a yellow solution, from which crystals may be obtained by evaporation: these consist of potassa in combination with a peculiar acid, which from the yellow colour of its salts has been called *croconic acid*. To obtain this acid the purified crystals of croconate of potassa are powdered and put into absolute alcohol, to which sulphuric acid (sp. gr. 1.78) is carefully added, so as barely to saturate the alkali. The yellow alcoholic solution is then poured off the precipitated sulphate of potassa, and the croconic acid obtained by evaporation. It is soluble in water, and yields prismatic crystals

of a yellow colour, astringent taste, and which redden litmus: it is not decomposed at a heat of 212° , but at high temperatures it deposits pure charcoal. Gmelin considers this acid as a compound of 5 atoms of carbon and 4 of oxygen, with apparently a small proportion of hydrogen, which, however, is less than 1 atom.

Anhydrous croconate of potassa is yellow and opaque; its crystals are orange-coloured prisms, transparent, inodorous, tasting like saltpetre; moderately soluble in cold, and very soluble in hot water, and insoluble in absolute alcohol: heated nearly to redness the salt suddenly glows throughout, rapidly evolving carbonic acid with a little carbonic oxide, and leaving a residue of carbonate of potassa and charcoal.

The attraction of potassium for oxygen, under most circumstances, exceeds that of all other bodies; it is consequently one of the most powerful deoxidizing agents which we possess. It forms two definite compounds with oxygen, which we may call the *protoxide* and *peroxide*; Berzelius admits a *suboxide*, but it is probably a mixture of potassium with the protoxide. When potassium is thrown upon water it takes fire, hydrogen gas is evolved, and a solution of *protoxide of potassium*, or *potassa*, is formed. When plunged under water, the potassium decomposes it with explosive violence, but without ignition, and the volume of the hydrogen evolved may be assumed as the equivalent or indicator of the proportion of oxygen transferred to the metal; 100 parts of potassium are thus found to absorb 20 of oxygen; and if this be considered a protoxide, then 20 : 100 :: 8 : 40,—so that 40 will be the number representing potassium (39·3 GRAHAM, 39·15 TURNER), and the *protoxide* or *potassa*, in its dry or anhydrous state, consists of

				Berzelius.	Davy.	Gay Lussac and Thenard.
Potassium	1	40	83·33	83·05	85	83·371
Oxygen	1	8	16·67	16·95	15	16·629
Potassa	1	48	100·00	100·00	100	100·000

The equivalent of potassium, deduced from the analysis of the chloride of potassium by Berzelius, is 39·15; he also states that 100 of potassium combine with 20·412 of oxygen; so that upon these data, the equivalent of potassium would be between 39 and 40. Mr. F. Penny, in his paper "on the application of the conversion of chlorates and nitrates into chlorides, and of chlorides into nitrates, to the determination of several equivalent numbers," arrives at the conclusion that 39·08 is the equivalent of potassium. (*Phil. Trans.*, 1839, p. 13.)

Potassa, in the state it is usually met with in laboratories under the name of *caustic potash*, contains a considerable portion of water, as is rendered manifest by the action of iron upon it at high temperatures, which occasions the evolution of hydrogen; and there always remains in the gun-barrel, after the above-described experiment, a portion of *dry potassa* combined with oxide of iron. To obtain dry potassa, or *anhydrous protoxide of potassium* in its pure state, the metal may be exposed, at common temperatures, to the action of perfectly dry air or oxygen; or 1 part of potassium may be fused with 1·4 of hydrate of potassa. It is a gray substance, fusible at a red heat, and volatile when heated to whiteness in the air. It combines very energetically with water to produce a *hydrate*, and what is commonly called *pure potassa*, is, in fact, this hydrate, composed of

							Berzelius.
Potassa	. . .	1	. .	48	. .	84.2	. . 84
Water	. . .	1	. .	9	. .	15.8	. . 16
<hr/>							
Hydrate of potassa	1			57		100.0	100

HYDRATED PROTOXIDE OF POTASSIUM, OR CAUSTIC POTASSA, (P+Q,) is procured in our laboratories by decomposing carbonate of potassa by lime. The best process consists in boiling in a clean iron vessel pure carbonate of potassa, with half its weight of pure quick-lime, in six or eight parts of water. The lime, which may be previously slaked, is

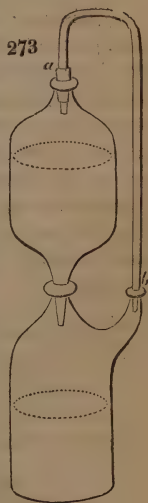
gradually added to the boiling alkaline solution, which is kept constantly stirred, and towards the end of the operation it is tested, by filtering a small portion, and pouring it into three or four times its bulk of dilute nitric acid: if there be no effervescence, sufficient lime has been used; but if carbonic acid escapes, the ebullition with lime must be continued until the tested portion shows no signs of carbonic acid. The whole is then allowed to remain quiet, that the carbonate of lime and excess of the hydrate of lime may subside; the clear liquor or *ley* may then be siphoned off, concentrated by evaporation, strained through a clean calico filter, and set by in a well-stopped bottle till it admits of being decanted, perfectly clear from any sediment. The clear solution is to be evaporated in a polished iron or pure silver basin, till it assumes the appearance of an oily liquid and concretes on cooling. It is often cast into sticks for the use of surgeons, who employ it as a caustic, and in this state it generally contains some peroxide and other impurities, and evolves oxygen and deposits a sediment when dissolved in water. It is the *potassa fusa* of the *London Pharmacopeia*. Having obtained the fused caustic potassa by lime, it may be further purified by boiling it in a silver basin with highly-rectified alcohol for a few minutes, and then setting it by in a stopped phial; when the impurities are deposited, the alcoholic solution may be poured off and rapidly evaporated to dryness in a silver vessel; or if the quantity of alcohol be considerable, it may be distilled off in a silver alembic with a glass head: the heat may then be raised so as to fuse the potassa, which on cooling should be broken up and preserved in well-closed phials.

Thus purified, hydrate of potassa is white, somewhat crystalline in texture, very acrid and corrosive, fusible at a heat below redness, and evaporates from an open vessel, at a bright-red heat, in the form of acrid fumes. At a white heat it is decomposed by charcoal, and carburetted hydrogen, carbonic oxide, and potassium, are formed. It quickly absorbs moisture and carbonic acid from the air, and is soluble in half its weight of cold water. When reduced to powder and slightly moistened it forms a crystallized combination which is said to be a terhydrate ($P + 3q$). By keeping a strong aqueous solution of potassa at a low temperature in a stopped phial, octoëdral and tabular crystals may be obtained which are stated to be a definite pentahydrate ($P + 5q$). It is highly alkaline, powerfully reddening turmeric, and converting several vegetable blues to green: and by a strong solution of it these colours are almost destroyed. It also acts energetically upon the greater number of organic products, and unites with the fat oils to form soap, hence the term *soap-lye*. Being generally and indeed almost exclusively procured from vegetables, it was formerly called *vegetable alkali*; but it also exists in certain minerals, and in a few animal secretions. Fuchs says that it may be economically obtained from certain varieties of felspar: for this purpose they are calcined with lime, then left for some time in contact with water, and the liquor filtered and evaporated. He says he has thus procured 19 per cent. from felspar and 15 from mica. When touched with moist fingers caustic potassa has a soapy feel, in consequence of its action upon the cuticle, and it then exhales a peculiar odour; this is also perceptible in the solution of potassa, and is probably referable to traces of organic matter acci-

dentally present. In the fused state it produces heat when dissolved in water; but in its crystallized state it excites considerable cold, especially when mixed with snow. At a natural temperature of 30° , Lowitz found that equal weights of crystallized potassa and snow depressed the thermometer 45° . (*Ann. de Chim.*, xxii.) It dissolves sulphur and several sulphurets, and alumina and silica. The oxides of manganese, zinc, tin, lead, antimony, cobalt, arsenic, molybdenum, tungsten, and nickel, are also soluble in aqueous solution of potassa.

The *Liquor Potassæ* of the Pharmacopœia is directed to be prepared as follows:—"Take of carbonate of potassa 15 ounces, lime 8 ounces, boiling distilled water a gallon. Dissolve the carbonate in half a gallon of the water; sprinkle a little of the water upon the lime in an earthen vessel, and the lime being slaked add the rest of the water. The liquors being immediately mixed together in a close vessel, shake them frequently until they are cold; then set the mixture by that the carbonate of lime may subside. Lastly, having poured off the supernatant liquor, keep it in a well-stoppered green glass bottle." Its specific gravity is 1.063.

Whilst a solution of caustic potassa is filtering, it is apt to absorb a little carbonic acid from the air, which may be prevented, upon the small scale, by covering the funnel with a plate of glass, and receiving it into a bottle as nearly air-tight as possible; or the annexed filtering apparatus, fig. 273, contrived by Mr. Donovan (*Annals of Philosophy*, xxvi. 115), may be used. It consists of two glass vessels connected by a tube, made air-tight by perforated corks at the junctions *a* and *b*. The upper vessel containing the solution to be filtered, terminates in a conical pipe, ground into the lower one, and into which is stuffed a piece of coarse linen.



In all cases where solutions of potassa are employed, it must be recollected that they gradually act upon glass, especially upon common white glass; hence green glass vessels are preferable: but where alkaline solutions are to be exposed to heat, or evaporated to dryness, even these communicate some impurity, and in such cases vessels of pure silver can only be relied upon, for they exert more or less action upon almost all the other metals, platinum not excepted.

The solution of caustic potassa is also frequently impure from the presence of carbonic acid, silica, alumina, lime, and sulphuric or hydrochloric acid. If nitric acid cause an effervescence when dropped into it, it indicates *carbonic acid*; if a gelatinous precipitate, not soluble in very slight excess of acid, it is *silica*; if soluble, it is *alumina*. The presence of *lime* is shown by adding oxalate of ammonia to the solution previously neutralized by nitric acid: in the same solution, nitrate of silver will indicate hydrochloric acid, or *chlorine*, and nitrate of baryta, *sulphuric acid*, or *sulphates*.

It may sometimes be useful to know the quantity of real potassa contained in watery solutions of different specific gravities; the following are the results of Dalton's experiments, in reference to this question:—

Specific Gravity.	Potassa per Cent.	Boiling Point.	Specific Gravity.	Potassa per Cent.	Boiling Point.
1.68 . .	51.2 . .	329°	1.33 . .	26.3 . .	229°
1.60 . .	46.7 . .	290	1.28 . .	23.4 . .	224
1.52 . .	42.9 . .	276	1.23 . .	19.5 . .	220
1.47 . .	39.6 . .	265	1.19 . .	16.2 . .	218
1.44 . .	36.8 . .	255	1.15 . .	13 . .	215
1.42 . .	34.4 . .	246	1.11 . .	9.5 . .	214
1.39 . .	32.4 . .	240	1.06 . .	4.7 . .	213
1.36 . .	29.4 . .	234			

PEROXIDE OF POTASSIUM. ($p + 3o$).—When potassium is burned in a silver spoon in oxygen gas, a yellow fusible substance is obtained, which, on cooling, acquires a scaly crystalline appearance. It consists, according to Gay Lussac and Thenard, of

				Gay Lussac and Thenard.
Potassium	1	40	62.5	65
Oxygen	3	24	37.5	35
Peroxide of potassium	1	64	100.0	100

This substance has some singular properties; it supports the combustion of most of the inflammables, and when heated in hydrogen, diminishes the bulk of the gas, and forms water: it decomposes ammonia under the same circumstances. When put into water, oxygen gas is evolved, and a solution of potassa obtained. When hydrate of potassa is fused in an open crucible, a portion of its water is disengaged, and oxygen absorbed, so as to form this peroxide; and hence it is, that common caustic potassa almost always effervesces, and gives out oxygen upon the affusion of water. When potassium is dropped into melted nitre, the peroxide is also formed; likewise by passing oxygen over potassa heated to redness.

POTASSIUM AND CHLORINE. CHLORIDE OF POTASSIUM. ($po + c$) or KCl.—Potassium burns brilliantly in chlorine, especially if introduced into the gas in the state of fusion, as, otherwise, a crust of chloride is apt to form and protect the interior from further action. This compound, formerly called *muriate of potash*, consists of

				Ure.
Potassium	1	40	52.6	53
Chlorine	1	36	47.4	47
Chloride of potassium	1	76	100.0	100

When potassium is heated in gaseous hydrochloric acid, chloride of potassium is formed, and hydrogen evolved; an experiment already adverted to under the article *Hydrochloric Acid* (p. 396). It is also formed by dissolving potassa or its carbonate in hydrochloric acid, and evaporating to dryness.

Chloride of potassium dissolves in three parts of water at 60°, or, according to Gay Lussac, 100 parts of water at 32° dissolve 29.23, and for every 1.8° above 32, the water takes up 0.2738 more of the salt. One part of the powdered salt stirred into four parts of cold water produces a depression of temperature of between 20° and 25°, whereas chloride of sodium under the same circumstances only depresses the ther-

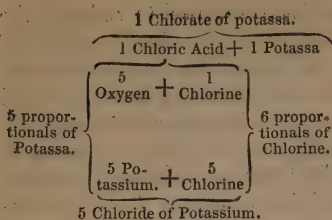
mometer between 2° or 3° , hence it has been proposed to estimate the relative proportions of these chlorides when mixed, by the depression of temperature resulting from their solution. Chloride of potassium crystallizes in cubes, which are anhydrous; its taste is saline and bitter. In old pharmacy it was called *digestive salt of Sylvius*; also, *regenerated sea-salt*. It is insoluble in alcohol. When intensely heated in open vessels, it evaporates in the form of white fumes. This salt is a residue of several chemical and pharmaceutical processes, and is sometimes found in considerable quantities in rough salt-petre, where it is often mistaken for common salt; it is also contained in kelp: the manufacturers of alum occasionally employ it as the source of potassa in that salt.

CHLORATE OF POTASSA $(p + o) + (c + 5o)$ or $(P + c')$ or $\overset{\cdot\cdot}{\underset{\cdot\cdot}{K}} \overset{\cdot\cdot}{\underset{\cdot\cdot}{C}} \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}_3$, is formed by passing chlorine through a solution of potassa. Chloride of potassium is one of the results, the other is *chlorate of potassa*, a salt in brilliant rhomboidal tables (formerly called *oxymuriate of potash*). Its crystalline forms have been described by Mr. Levy (*Quarterly Journal*, xv. 286), and by Mr. Brooke (*Ann. Phil.*, v. 451): they belong to the oblique prismatic system.

This salt is prepared, upon the large scale, by charging one or two Woulfe's bottles with a strong solution of carbonate of potassa, and passing chlorine slowly through it at the lowest convenient temperature: the gas is absorbed, and the liquor effervesces, chiefly from the escape of carbonic acid; when this has ceased, the liquor may be put aside in a cold dark place for about 24 hours, when it will be found to have deposited a considerable portion of the crystallized chlorate, which may be taken out, drained, and purified by solution in hot water, which, during cooling, again deposits the salt in white crystalline scales. The mother-liquor, from which more of the salt may be obtained by evaporation, is generally of a pinkish tint, from the presence of a trace of manganese; but this tint disappears when sufficiency of chlorine has been passed in to saturate it, and it acquires a brownish hue*. Solution of pure potassa absorbs the gas more readily than the carbonate, but nearly with the same phenomena, and in either case care must be taken that the tube conveying the chlorine does not become stopped up by the salt, which is apt to happen if it be not sufficiently capacious. To understand the theory of this process we must recollect that chloric acid is a compound of one proportional of chlorine and five of oxygen, and that chloride of potassium consists of one proportional of chlorine and one of potassium, and that potassa contains one proportional of oxygen and one of potassium: it follows, then, that five proportionals of chlorine acting upon five of potassa will expel five of oxygen, which, uniting with one of chlorine, will form one proportional of chloric acid, and this uniting to a proportional of undecomposed potassa will form chlorate of potassa, as shown in the following diagram:—

* In this process, the carbonic acid is expelled when excess of chlorine is passed into the solution: by particular management chlorine may be retained

in a solution of carbonated alkali, forming a peculiar compound of chlorine, or hypochlorous acid, and potassa. See *Carbonate of Soda*.



It appears, therefore, that five proportionals of potassa will require six of chlorine to be consumed in the formation of five proportionals of chloride of potassium, and one proportional of chloric acid. The elements of the water are not concerned in the formation of these products, but that fluid performs the important office of en-

abling the different elements to act upon each other in their nascent states.

According to Löwig, chloride of lime, which by long keeping has lost much of its bleaching power, contains chlorate of lime, and may be used for the preparation of chlorate of potassa: the solution of the lime salt is boiled in order to complete the conversion of the chloride into chlorate, and then partially decomposed by carbonate of potassa, or evaporated with an admixture of chloride of potassium, when chlorate of potassa crystallizes, and chloride of calcium remains in solution. (GRAHAM.)

Chlorate of potassa is an anhydrous salt of a cooling and austere taste. Its specific gravity is 1.989. (HASSENFRATZ.) When pure, its aqueous solution is not rendered turbid by nitrate of silver. When triturated, it appears phosphorescent. It decrepitates and fuses at a temperature between 400° and 500° : at a higher heat it effervesces, and gives out nearly 40 *per cent.* of its weight of oxygen, and chloride of potassium remains. It is soluble in 18 parts of cold and 2.5 of boiling water; or, according to Gay Lussac, 100 parts of water at 32° dissolve 3.5 parts, at 59° 6 parts, at 95° 12 parts, at 120° 19 parts, and at 216° , which is the boiling-point of the saturated solution, 60 parts. It acts very energetically upon many inflammables, and triturated with sulphur, phosphorus, and charcoal, produces inflammation and explosion. A mixture of three parts of this chlorate with one of sulphur, detonates loudly when struck upon an anvil with a hammer, and even sometimes explodes spontaneously; hence it should not be kept ready mixed. Chlorate of potassa was proposed by Berthollet as a substitute for nitre in gunpowder. The attempt was made at Essone in 1788: but, as might have been expected, no sooner was the mixture of the chlorate with the sulphur and charcoal submitted to trituration, than it exploded with violence, and proved fatal to several persons. With phosphorus the detonation is dangerously violent; the experiment is best made, by wrapping a grain of phosphorus and two of the chlorate in a small piece of paper, and striking them a blow with a hammer, upon an anvil. The phosphorus is generally thrown about in an inflamed state. These phenomena depend upon the sudden decomposition of the chloric acid.

The action of sulphuric acid upon chlorate of potassa has already been adverted to. (See *Peroxide of Chlorine*, p. 368.) If, instead of distilling the yellow mixture of the acid and chlorate with the caution there described, it be heated to about 212° , it suddenly explodes. The theory of the production of chloric oxide is more explicitly described in the next article.

When sulphuric acid is dropped upon mixtures of this salt and combustibles, instant ignition ensues in consequence of the evolution of per-

oxide of chlorine. A mixture of sugar and the chlorate thus treated, is immediately kindled, with a red and blue flame; and a mixture of sulphuret of antimony and the salt suddenly deflagrates with a bright puff of flame and smoke: the latter mixture requires to be cautiously made, as it often takes fire by mere trituration. Matches tipped with some of these inflammable mixtures, and called *Lucifers*, are now in common use, and are inflamed either by friction or by the contact of sulphuric acid, which is most conveniently applied by putting some asbestos into a small well-stopped phial, and moistening it with sulphuric acid; the match is rapidly dipped into the phial and inflames on touching the asbestos, without the risk of spirting about the acid. Some of the matches which inflame by a pinch or blow, contain a portion of a drop of sulphuric acid hermetically sealed in a piece of very small and thin glass tube, and which escapes when broken, and acts upon the inflammable mixture. Berzelius gives the following as the best composition for the match: 30 parts of powdered chlorate of potassa, 10 of powdered sulphur, 8 of sugar, 5 of gum-arabic, and a little cinnabar. The sugar, gum, and salt, are first rubbed together into a paste with a sufficiency of water; the sulphur is then added, and the whole being thoroughly beaten together, small brimstone matches are dipped in, so as to retain a thin coat of the mixture upon their sulphuretted points: they should be quite dry before they are used. Some of the recently-improved lucifer matches appear to contain phosphorus; they inflame by slight friction upon emery paper or any hard rough substance. One of the compounds occasionally employed in percussion gun-locks is a similar composition: 10 parts of gunpowder are rubbed with water, and the soluble part poured off; the remaining paste is then mixed with $5\frac{1}{4}$ parts of finely-powdered chlorate of potassa, and a drop of it put into each of the small copper caps adapted to the peculiar tubular touch-hole of the gun; a blow being struck upon the cap the powder is inflamed, and communicates to that in the barrel. The great disadvantage of this compound is, that it forms products which soon rust the touch-hole and surrounding parts: fulminating mercury is, therefore, now generally substituted.

When sulphuric or nitric acids are poured upon mixtures of chlorate of potassa and certain combustibles under water, by means of a long funnel, inflammation also ensues. In this way a beautiful experiment may be made with phosphorus, a few small pieces of which are put at the bottom of a tall glass of water, and a little of the chlorate thrown in upon it; sulphuric acid is then carefully introduced into the contact of the salt by a funnel, with a tube long enough to reach to the bottom of the glass; the phosphorus presently inflames and burns vividly in different parts of the fluid, forming a kind of well of fire. A few grains of chlorate of potassa put into a teaspoonful of hydrochloric acid, and then diluted with water, form an extemporaneous bleaching-liquor.

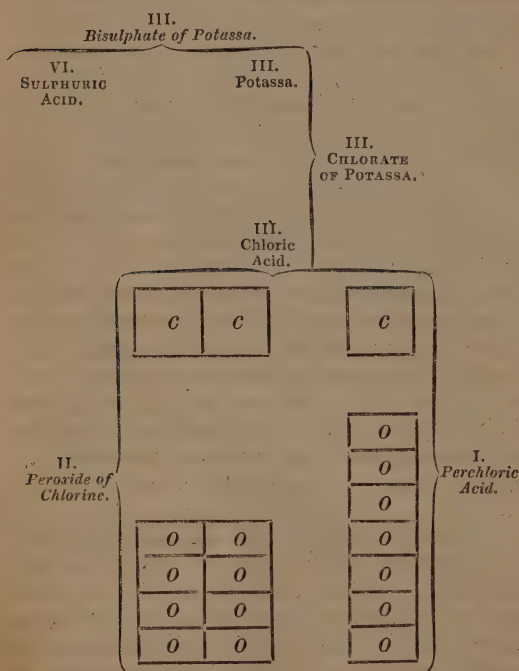
The ultimate elements of chlorate of potassa are

Oxygen . . .	6	. . .	48	. . .	33.71
Chlorine . . .	1	. . .	36	. . .	29.03
Potassium . . .	1	. . .	40	. . .	32.26
	<hr/>		<hr/>		<hr/>
	1		124		100.00

Or it consists of

Potassa	. . . 1	. . . 48	. . . 38.70	Berzelius.
Chloric acid	. . . 1	. . . 76	. . . 61.30	38.49
<hr/>		<hr/>	<hr/>	<hr/>
Chlorate of potassa	1	124	100.00	100.00

OXYCHLORATE OR PERCHLORATE OF POTASSA ($p+o$) + ($c+7o$) or ($P+c''$) or $\overset{\cdot\cdot\cdot}{\text{K}} \overset{\cdot\cdot\cdot}{\text{C}}$, may be formed by moistening one part of chlorate of potassa with three of sulphuric acid, and subsequently *carefully* warming the mass till it becomes white, and the oxide of chlorine is expelled: in this state it consists of bisulphate and perchlorate of potassa, which may be separated by solution and crystallization, the former being much more soluble in cold water than the latter salt.



In reference to the production of peroxide of chlorine and perchloric acid, as the result of the action of sulphuric acid upon chlorate of potassa, the annexed diagram may, perhaps, be useful. The original substances are printed in capitals, the components in common type, and the resulting compounds in italics; the volumes of oxygen and of chlorine being shown by the usual symbols of bulks which I have elsewhere employed. The Roman numerals denote the number of proportionals or equivalents presumed to be employed or formed.

Thus it appears that 6 proportionals of sulphuric acid acting upon 3 of chlorate of potassa form 3 of bisulphate of potassa, and detach 3 of chloric acid, the elements of which are 3 of chlorine and 15 of oxygen: of these, 2 proportionals of chlorine and 8 of oxygen form 2 of peroxide of chlorine; and the remaining 1 of chlorine and 7 of oxygen form perchloric acid. If instead, as in the above diagram, of considering the mere formation of perchloric acid, we refer to the formation of perchlorate of potassa, we must assume that the oxygen is transferred to the chloric acid of an undecomposed portion of chlorate of potassa, and so converts it into perchlorate.

Perchlorate of potassa does not change vegetable colours, nor is it altered by exposure to air. It crystallizes in small octoëdra with square bases. It requires rather more than 50 parts of water at 60° for its solution: but is much more soluble in boiling water. It is insoluble in alcohol: it detonates slightly when rubbed with sulphur. When mixed with its own weight of sulphuric acid, and distilled at 280°, solution of oxychloric acid passes over. It may be decomposed by exposure to a temperature of 412°. Oxygen is given off, equal to 0·45 per cent. of the weight of the salt, and chloride of potassium remains in the retort.

Gmelin states that when a saturated solution of chlorate of potassa is exposed to the decomposing agency of Voltaic electricity, transmitted by platinum poles, crystals of oxychlorate of potassa are formed at the positive pole, whilst hydrogen is evolved at the negative.

The ultimate elements of this salt are

Oxygen	8	.	.	64	.	.	45·7
Chlorine	1	.	.	36	.	.	25·7
Potassium	1	.	.	40	.	.	28·6
	1			140			100·0

Its proximate composition:

Potassa	1	.	.	48	.	.	34·3	.	.	Stadion.
Perchloric acid	1	.	.	92	.	.	65·7	.	.	34·31
					1			140			100·0			65·69
Perchlorate of potassa					1			140			100·0			100·00

IODIDE OF POTASSIUM. (*po + i*) or K I.—Iodine and potassium act upon each other very energetically, evolving heat and light, and a crystalline compound is obtained, white and fusible. When hydriodic acid is saturated by potassa, and the solution carefully evaporated, anhydrous prismatic crystals of the iodide (or as it is sometimes called *hydriodate of potassa*) are obtained. The readiest mode of procuring this compound consists in dissolving iodine in solution of potassa, till it begins to assume a brown colour; on evaporating to dryness, and fusing the residuary salt, a pure iodide of potassium remains. If, instead of fusing the products, the solution be carefully evaporated nearly to dryness, and alcohol poured upon it, the iodide is dissolved, and there remains a salt insoluble in alcohol, which is *iodate of potassa*, and which, at a red heat, evolves oxygen, and becomes iodide of potassium. The action of iodine upon the alkali appears in all respects to correspond with that of chlorine. Iodide of potassium is also frequently prepared by decomposing a solution of iodide of zinc by carbonate of potassa, and filtering off and evaporating the resulting solution of the iodide, which, however, is apt to retain iodide of zinc. The Pharmacopœia directs the decomposition of a solution of iodide of iron by carbonate of potassa, but in this case all traces of iron are very difficultly got rid of. Iodide of potassium forms cubic and prismatic crystals, which are deliquescent in very damp air. According to Gay Lussac, 100 parts of water at 65° dissolve 143 of this salt, and a considerable depression of temperature is produced during the solution; it is sparingly soluble in absolute alcohol, but much more so in alcohol, sp. gr. 850. It is pretty largely used in medicine, and as it occurs in commerce is frequently mixed with chloride of potassium and sodium,

and with sulphate and carbonate of potassa. It should be purchased in crystals, which ought not to be very deliquescent, and should perfectly dissolve in six or eight parts of alcohol, sp. gr. '836. They generally redden turmeric from the presence of a little adhering carbonate of potassa.

Iodide of potassium consists of

Potassium	1	40	24	Gay Lussac. 23·8
Iodine	1	126	76	76·2
<hr/>		<hr/>	<hr/>	<hr/>
Iodide of potassium	1	166	100	100·0

The aqueous solution of iodide of potassium dissolves a considerable portion of iodine; this solution, under the name of *ioduretted iodide of potassium*, is sometimes used in medicine: it is of a deep-brown colour. According to Baup a saturated solution of iodide of potassium will dissolve two equivalents of iodine, one of which falls on diluting the solution.

IODATE OF POTASSA $(p+o) + (i+5o)$ or $P+i'$, obtained as just described, is a white, difficultly soluble salt, requiring about 14 parts of water at 60° for its solution: at a red heat, it gives out between 22 and 23 *per cent.* of oxygen, and is converted into iodide of potassium. Iodide of potassium may also be converted into iodate of potassa, by fusing it in a crucible, and projecting upon it rather less than twice its weight of chlorate of potassa: warm water removes the chloride of potassium and leaves the iodate.

This salt is insoluble in alcohol: it forms small and permanent prismatic crystals, soluble without decomposition in warm sulphuric acid, and detonating with a purple flame when thrown upon hot coals. With the addition of potassa, it yields a crystallizable subsalt, the exact composition of which has not been determined; it is very soluble.

Iodate of potassa consists of

Potassa	1	48	22·54
Iodic acid	1	166	77·46
<hr/>		<hr/>	<hr/>
Iodate of potassa	1	214	100·00

Serullas has described a *biniodate* and a *teriodate* of potassa. (*Ann. de Ch. et Ph.*, xliii. 113.) The biniodate is obtained by adding an additional equivalent of iodic acid to a solution of the neutral iodate saturated at a high temperature: it forms prismatic crystals with diëdral summits, which retain an equivalent of water, but which, according to Graham, may be rendered anhydrous by heat: it is soluble in 75 parts of water at 60° . The *teriodate* is formed when a strong acid is added to a hot saturated solution of the neutral iodate, and allowing it to cool slowly: it forms rhomboëdral crystals soluble in 25 parts of water. According to Serullas the biniodate of potassa has a great tendency to form double salts; one of these, with *chloride of potassium*, is obtained in crystals, when a little hydrochloric acid is added to a solution of iodate of potassa and the mixture subjected to spontaneous evaporation: it contains 1 atom of the biniodate with 1 of chloride; it cannot be formed by the direct union of its component salts, and is decomposed by water. Another double salt of biniodate with *bisulphate of potassa* is obtained from the mother liquor

which remains when teriodate of potassa is prepared by means of sulphuric acid; it forms crystals which are decomposed by water, and, like the preceding, cannot be formed directly.

BROMIDE OF POTASSIUM. ($po + b$) or K B.—Potassium and bromine act intensely upon each other, evolving heat and light, and producing explosion. When bromine is dropped into solution of potassa, the mixture evaporated, and the residue heated to redness, *bromide of potassium* is also obtained; it is white, fusible, and crystallizes in cubes, easily soluble in water, and slightly so in alcohol. It consists of

Potassium	1	. .	40	. .	33.9
Bromine	1	. .	78	. .	66.1
<hr/>						
Bromide of potassium		1		118		100.0

It is prepared for medical use, either by the above process, or by decomposing bromide of zinc or bromide of iron, by carbonate of potassa; it should be purchased in crystals, as it is otherwise apt to be impure.

When ethereal solution of bromine is agitated with liquid potassa, the yellow colour disappears, and bromate of potassa and bromide of potassium are the results. The action, therefore, of bromine is here analogous to that of chlorine and iodine.

BROMATE OF POTASSA ($po + o$) + ($b + 5o$) or ($P + b'$) separates in the form of a crystalline powder, when bromine and solution of potassa are mixed in sufficient quantities. It scintillates on a hot coal, like nitre, and evolving oxygen becomes bromide of potassium. It is slightly soluble in alcohol, readily soluble in water, and crystallizes in needles: mixed with sulphur it detonates by a blow. Its solution occasions a white precipitate in nitrate of silver. (BALARD, *Quarterly Journal*, xxii. 389.)

FLUORIDE OF POTASSIUM. ($po + f$).—When hydrofluoric acid is saturated with potassa, and evaporated to dryness, a deliquescent and very difficultly crystallizable compound is obtained, which must be regarded as a *fluoride of potassium*. It probably consists of

Potassium	1	. .	40	. .	68.965
Fluorine	1	. .	18	. .	31.034
<hr/>						
Fluoride of potassium		1		58		100.000

This fluoride bears an intense heat without change.

Berzelius has described an apparently peculiar compound, obtained by dissolving the above fluoride in hydrofluoric acid, and evaporating to dryness in a platinum vessel: it is crystallizable, readily soluble in water, and when heated to incipient redness is decomposed, hydrofluoric acid being evolved, and fluoride of potassium remaining. It appears to consist of

						Berzelius:
Fluoride of potassium	1	. .	58	. .	75.3	. . 74.9
Hydrofluoric acid	1	. .	19	. .	24.7	. . 25.1
<hr/>						
	1		77		100.0	100.0

POTASSIUM AND HYDROGEN.—When potassium is heated in hydrogen, it absorbs a portion of the gas, and produces a gray infusible *hydruret*,

destitute of lustre, and burning vividly when heated in air or oxygen gas. When heated, *per se*, it evolves hydrogen; and the same change takes place in the contact of mercury. When hydrogen and potassium are passed together through a white-hot tube, the gas dissolves the metal, and produces a spontaneously inflammable *potassiuretted hydrogen gas*. Potassiuretted hydrogen is also produced when potassium is thrown upon water, and is the cause of the red flame and white fumes produced during its combustion under such circumstances. Both these compounds are usually formed during the operation for obtaining potassium by the gun-barrel. (GAY LUSSAC and THENARD.)

NITRATE OF POTASSA. NITRE. SALTPETRE. $(po + o) + (n + 5o)$ or $(P + n')$, or $KO NO_5$, or $K \ddot{N}$.—This salt is an abundant natural product, and is principally brought to this country from the East Indies, where it is produced by lixiviation from certain soils. The greater part of the rough nitre imported from the East Indies is in broken crystals of a brown colour, and more or less deliquescent; exclusive of other impurities, it often contains a very considerable portion of common salt, which, re-acting upon the nitre, induces the production of a portion of nitrate of soda and chloride of potassium. It also usually contains sulphate of lime, and often evident traces of organic matter.

In Germany and France it is artificially produced in what are termed nitre-beds. Thenard (*Traité de Chimie Élémentaire*) has described the French process at length. (See also DUMAS, *Chim. App. aux Arts*, ii., and KUHLMAN, *Mem. Acad. Sciences de Lille*, 1838; also LIEBIG's *Ann.*, xxix. 272.) It consists in lixiviating old plaster rubbish, which, when rich in nitre, affords about five per cent. Refuse animal and vegetable matter, which has putrified in contact with calcareous soils, produces nitrate of lime, which affords nitre by mixture with carbonate of potassa. In the same way it is abundantly produced in some parts of Spain. Exudations, containing saltpetre, are not uncommon upon new walls, where it appears to arise from the decomposition of animal matter contained in the mortar. It was long ago shown by Glauber, that a vault plastered over with a mixture of lime, wood-ashes, and cows' dung, soon becomes covered with efflorescent nitre, and that, after some months, the materials yield, on lixiviation, a considerable proportion of that salt.

The loss which rough nitre sustains in refining, is technically termed the *refraction*, and can only be ascertained by analysis, which frequently is somewhat difficult and intricate: it is, moreover, not easy to get a fair sample of a cargo. The samples which the merchants and brokers select for analysis, generally consist of portions drawn from each bag and afterwards mixed together, and if carelessly or unfairly taken, or exposed so as to become more moist or more dry than the bulk, the report of the analyst is often unsatisfactory. He should work upon not less than 25 to 50 lbs. of such sample, which should be ground or triturated so as to produce a properly uniform mixture of the whole, for it often includes lumps of pure nitre or of other salts; of this uniform mixture a portion is then taken for analysis. The moisture is determined by the loss occasioned by drying a given weight on the sand-bath. A portion is then dissolved

in water and tested, so as to acquire some general notion of the impurities; and, from the effect of nitrate of silver, nitrate of baryta, and oxalate of ammonia, the presence of chlorides, sulphuric acid, and lime, is determined: the lime is generally in the state of sulphate, and more or less sulphate of potassa is also usually present; the chlorine is chiefly derived from the chlorides of potassium and sodium. Another portion of the sample should be dissolved in about thrice its weight of boiling water, and filtered, by which the sand and other insoluble impurities are collected; the salt should then be crystallized in the usual way, during which the appearances and forms of the successive deposits will indicate, to the experienced eye, the nature of the foreign salts present; among which nitrate of soda, sulphate of potassa, sulphate and nitrate of lime, and chloride of sodium and potassium, with traces of chloride of calcium, and sometimes of a peculiar organic matter, are frequently found. It will be obvious that the accurate quantitative analysis of such a mixture of salts is not a very easy problem, and yet the separation of nitrate of soda from nitrate of potassa, and of chloride of potassium from chloride of sodium, are essential steps, inasmuch as the value of the sample is materially affected by their relative proportions: for nitrate of soda, to say nothing of its unfitness for the manufacture of gunpowder, is cheaper than nitrate of potassa; and chloride of sodium is of no value, whilst chloride of potassium is purchased by the alum-makers; so that a sample of nitre, containing the latter salt, is in this respect worth more than where it only contains common salt. But inasmuch as the equivalent of chloride of sodium is only 60, and that of chloride of potassium 76, it is obvious that if the whole of the chlorine, as indicated by the weight of the chloride of silver, be considered as in combination with sodium (part of the sample consisting of chloride of potassium), the refraction will be estimated below the mark. Hence the necessity of ascertaining the relative proportions of both chlorides, which is best effected by converting them into sulphates, and separating them by crystallization.

A rough method of determining the value of a sample of nitre, and which, in some cases, especially where common salt is the chief impurity, admits of considerable accuracy, consists in putting a pound of the salt in powder into a basin, and pouring upon it a pint of a saturated aqueous solution of pure nitre; this mixture is well stirred for 15 or 20 minutes, then left at rest, and when the salt is deposited, the liquor is poured off and filtered: half a pint of the saturated solution of pure nitre is then again poured upon the remaining salt, stirred as before, and then the whole contents of the basin are carefully transferred into the filter. In some cases where the quantity of common salt is excessive (exceeding 66 per cent.) the washing must be repeated a third time, but this is rarely necessary. When the dripping of the filter has ceased, it is carefully removed with its contents, from the funnel, and placed upon a few sheets of coarse filtering paper lying upon a chalk table or other absorptive substance, the saltpetre being carefully spread out so that the moisture may be absorbed. When it is dry enough to admit of removal, it must be carefully transferred into a basin placed upon a sand bath, and the drying completed till it no longer adheres to the rod or ivory knife with which it is stirred; it is then weighed, and the loss of weight, (as compared

with the sample,) gives the impurities; but from this, 2 *per cent.* should be deducted for the nitre deposited by the saturated solution whilst taking up the common salt. When the common process for refining nitre is conducted as follows, it may be made subservient to the more accurate analysis.

PURIFICATION OF NITRE.—A given quantity of the rough salt (say 7 lbs.) is accurately weighed, and then dissolved by heat in three or four parts of water; when boiling, the scum is removed until no more rises, and then the solution is allowed to settle for ten minutes or longer. In this way nearly all the dirt falls down, and the clear solution, being poured off, is passed through a filter of tow into a pan, and set aside to crystallize; the dirt left behind is added to the scum, and both being diluted, are filtered through paper, and the clear solution preserved. Next day the crystals formed in the pan are separated and put into funnels to drain, and the mother-liquor with the filtered solution from the scum, &c. are further evaporated, and again left to crystallize. On the second evaporation, impurities generally separate from the solution; these are sometimes oxide of iron, or sulphate of lime, but most frequently chloride of sodium and of potassium, sulphate of potassa, and nitrate of soda. The two first are easily separated by filtration; the chlorides are best separated by evaporating the solution considerably, until much salt has been deposited, and then pouring the whole upon a filter of tow; the common salt, with more or less of the others, will remain on it, and should be washed by water to separate the nitre, which water should be added to the liquor, and the whole then brought to the crystallizing point. When cold, the crystals deposited by this solution are to be separated as before, until the mother-liquor is divided into other salts and nitre. It frequently happens that the crystals from the two or three last evaporations are coloured or contaminated by the adhesion of common salt, sulphate of lime, &c.; in this case, they should be re-dissolved and re-crystallized with the same precautions as before. Care should be taken in drying the crystals, especially when large, that no water remain in the interstices or cleavages between them, which is often the case to a considerable extent; and not unfrequently the interstitial water retains foreign salts, so that, in purifying nitre upon the large scale, it is often advantageous to stir it whilst crystallizing, that the crystals may be small and broken, and then the adhering impurities may be better washed out by cold water. When pure, the solution of nitre is not rendered turbid either by nitrate of silver or nitrate of baryta.

Nitre crystallizes in six-sided prisms, usually terminated by dièdral summits. Its specific gravity is 1.933. Its primitive form is a right rhombic prism, the measurement and modifications of which have been given by Mr. Levy (*Quarterly Journal*, xv. 284). The crystals are large and smooth when obtained from a great mass of solution, but irregular and striated when formed in smaller quantities. The large crystals are very sensible to changes of temperature, and when handled generally crack transversely; so that it is difficult to preserve them entire. They are not altered by exposure to air. According to Bergman, nitre dissolves in 7 parts of water at 60°, and in its own weight at 212°; but these proportions are not correct: La Grange states that 1 part of nitre dissolves in between 3 and 4 of water at 60°, and in half its weight at 212°. Gay

Lussac has shown that the solubility of nitre varies extremely with temperature: at 32° , 100 parts of water dissolve 13.2 of the salt; at 77° , the salt dissolved by 100 of water is 38 parts; at 132° , it amounts to 97 parts; at 176° , to 169 parts; at 210° , to 236 parts; and at 212° , to 246 parts. According to Dr. Ure, the temperature of a saturated solution of nitre, boiling hot, is 340° , and the relation of the salt to its solvent is in weight as 3 to 1. Upon the same authority, water at 60° dissolves one-fourth its weight of nitre; or, more exactly, this saturated solution contains 21 per cent. of salt: its specific gravity is 1.1415; and 100 parts in volume of the two constituents occupy now 97.91 parts. (*Jour. Royal Inst.*, i. 121.) Berzelius observes, that the solubility of nitre is apparently increased by the presence of common salt, but that this arises from their mutual reaction, producing nitrate of soda and chloride of potassium. Yet, during crystallization, common salt and nitre separate distinctly from each other. During the solution of 1 part of powdered nitre in 5 of water, the temperature sinks from 50° to 35° . Its use in cooling mixtures has already been noticed, p. 169. It is insoluble in pure alcohol. The crystals of nitre, though the salt is anhydrous, generally contain interstitial water; so that they appear moist when powdered, and lose weight on drying. The taste of nitre is cooling and peculiar, and it is used in medicine in small doses, as a diuretic and sedative: in doses of from half an ounce to an ounce it is poisonous, exciting spasms, vomiting, bloody stools, convulsions, and often proving fatal. In such cases viscid mucilaginous drinks with opium and cordials are the most effective restoratives. This salt consists of

Potassa . . . 1 . . .	48 . . .	47.1 . . .	Wollaston, 46.668
Nitric acid . . . 1 . . .	54 . . .	52.9 . . .	53.332
<hr/>			
Nitrate of potassa 1	102	100.0	100.000

Its ultimate components are*,

Oxygen . . . 6 . . .	48 . . .	47.06
Nitrogen . . . 1 . . .	14 . . .	13.72
Potassium . . . 1 . . .	40 . . .	39.22
<hr/>		
Nitrate of potassa 1	102	100.00

At a temperature of about 600° , nitre fuses without undergoing change of composition, and congeals, on cooling, into a white striated mass. Sometimes it is cast into small balls or cakes, called *sal prunella*, a name said to be derived from the circumstance of its having been occasionally stained of a plum-colour. At a red heat, nitre is slowly decomposed; and if distilled in an earthen retort or gun-barrel, it affords abundance of oxygen gas, one pound yielding about 12,000 cubic inches, of sufficient purity for many common experiments in which that gas is used; it is of course mixed with a portion of nitrogen. In this decomposition the nitre is first converted into *hyponitrite of potassa*, which is deliquescent; and afterwards, according to Berzelius, compounds are formed of potassa with nitric and nitrous oxides.

* Professor Daniell has shown that in the electrolysis of a solution of nitre, the results indicate that an atom of potassium travels to the negative electrode, and an atom of nitrogen and six atoms of oxygen to the positive electrode; hence the electrolytic formula of nitre is $(n+6o)+po$. He calls it an *oxynitron of potassium*. (*Phil. Trans.*, 1839, p. 109, and 1840, p. 223.)

Nitre is rapidly decomposed by charcoal at a red heat; and the results are carbonic oxide and acid, nitrogen, and carbonate of potassa, formerly called *nitrum fixum*, and *white flux*. The old chemists used to perform this detonation in retorts connected with capacious receivers, which were generally blown to pieces; sometimes they succeeded in obtaining a little acidulated water, which they called *chlyssus of nitre*, and attributed to it wonderful medical virtues. These mixtures of nitre and charcoal form the basis of a variety of compositions used for fireworks, the rapidity of the combustion being modified by the relative proportion of the charcoal. When phosphorus is thrown upon nitre, and inflamed, a vivid combustion ensues, and a phosphate of potassa is formed. Sulphur sprinkled upon hot nitre burns, and produces a mixture of sulphate and sulphite of potassa, formerly employed in medicine, under the name of *Glaser's polychrest salt*. The combustion of a mixture of sulphur with a small quantity of nitre has already been described as the source of sulphuric acid (p. 463). When a mixture of two parts of nitre and one of hydrochlorate of ammonia are heated to redness, chloride of potassium, water, chlorine, hydrochloric acid, and a little nitrous acid, are the results, and nitrogen gas is copiously evolved. (SOUBEIRAN, *Journal de Pharmacie*, 1827, p. 321.) Most of the metals, when in filings or powder, detonate and burn when thrown on red-hot nitre; some of the more inflammable metals produce in this way a considerable explosion.

A mixture of three parts of nitre, two of dry carbonate of potassa, and one of sulphur, forms *fulminating powder*. If a little of this compound be heated upon a metallic plate, it blackens, fuses, and explodes with much violence, in consequence of the rapid action of the sulphur upon the nitre, and the sudden evolution of nitrogen in its gaseous form.

The action of sulphuric acid on nitre has been described above (p. 416), and will be again adverted to under *sulphate of potassa*. When nitre and hydrochloric acid are heated together, chlorine and nitrous acid are evolved, and on evaporation to dryness, chloride of potassium remains. Mr. Penny proposes this decomposition as the basis of a method of ascertaining the quantity of nitrate of potassa in crude saltpetre. (*Phil. Trans.*, 1839, p. 13.)

GUNPOWDER consists of a very intimate mixture of nitre, sulphur, and charcoal, the proportions varying, according to the uses made of it, as follow:—

	Common gunpowder.	Shooting powder.	Shooting powder.	Miners' powder.
Saltpetre	75.0	78	76	65
Charcoal	12.5	12	15	15
Sulphur	12.5	10	9	20

The following is a table of the composition of gunpowder of several countries:—

	Nitre.	Charcoal.	Sulphur.
Waltham Abbey mills	75	15	10
France, national establishment	75	12.5	12.5
— for sportsmen	78	12	10
— for mining	65	15	20
United States of America	75	12.5	12.5
Prussia	75	12.5	12.5
Russia	73.78	13.59	12.63

	Nitre.	Charcoal.	Sulphur.
Austria	76	11.5	12.5
Spain	76.47	10.78	12.75
Switzerland (round powder) . . .	76	14	10
Chinese	75	14.4	9.9

The ingredients are *perfectly* mixed, moistened, beaten into a cake, which is afterwards broken up, granulated, dried, and for the finest powder polished by attrition. The violence of the explosion of gunpowder depends upon the sudden production of gaseous matter, and of intense heat, resulting from the action of the combustibles upon the nitre. Carbonic oxide, carbonic acid, nitrogen, and sulphurous acid, are the principal gaseous results; and the solid residue consists of carbonate and sulphate of potassa, sulphuret of potassium, and charcoal. (CRUICKSHANKS, *Nicholson's Journal*, iv. See also the same *Journal*, xiii. 277.)

If we theoretically inquire how the maximum gaseous volume is to be produced from the chemical reaction of the elements of gunpowder, we shall find it to be by the generation of carbonic oxide and sulphurous acid, with the disengagement of nitrogen. This will lead to the following proportions of their constituents. (URE, *Journal Royal Institution*, vol. i. p. 135.)

		Per cent.
1 equivalent of nitre . .	102	75.00
1 " sulphur . .	16	11.77
3 " charcoal . .	18	13.23
	<hr/> 136	<hr/> 100.00

The nitre contains 5 proportionals of oxygen, of which 3 combining with 3 of charcoal will furnish 3 of carbonic oxide gas, while the remaining 2 will convert the 1 of sulphur into sulphurous acid gas: the single proportional of nitrogen is, therefore, in this view disengaged alone. The gaseous volume, on this supposition, evolved from 130 grains of gunpowder, equivalent in bulk to 75.5 grains of water, or to three-tenths of a cubic inch, will be at the atmospheric temperature as follows:

	Grains.	Cubic inches.
Carbonic oxide	42	141.6
Sulphurous acid	32	47.2
Nitrogen	14	47.4
	<hr/> 136	<hr/> 236.2

Being an expansion of one volume into 787.3. But as the temperature of the gases at the instant of their combustive formation must be incandescent, this volume may be safely estimated at three times the above amount, or considerably above two thousand times the bulk of the solid.

But this theoretical account of the gases developed does not exactly accord with the experimental products usually assigned, especially as relates to the evolution of carbonic acid, and to the residuary sulphuret of potassium; with these, the following view of the results of the deflagration given by Graham, is more consistent.

Before combustion.			After combustion.	
3 equivalents of carbon			} 3 carbonic acid	
1 " of nitre	{	6 oxygen . .		
		1 nitrogen . .		1 nitrogen
1 " of sulphur		1 potassium . .		
			} 1 sulphuret of potassium	

Carburetted and sulphuretted hydrogen, and vapour of water, often mentioned among the products of the combustion of gunpowder, are found in very minute quantities only, for good gunpowder does not contain more than 1 *per cent.* of water, which can be the only source of hydrogenated compounds. The larger the proportion of sulphur the less forcible will be the explosion of the powder; thus, when it contains 12 of charcoal and 12 of sulphur in 100, it does not throw a proof-shell so far as that containing 19 of charcoal and 9 of sulphur. But the former powder keeps better than the latter, so that for the supply of remote colonies and humid climates, it perhaps justifies a slight sacrifice of strength, which may be compensated by a larger charge. (For the details of the manufacture of gunpowder, see COLEMAN, *Phil. Mag.*, ix.; AIKIN'S *Dictionary of Chemistry* (article, GUNPOWDER); URE'S *Dictionary of Arts and Manufactures*; and DUMAS, *Chimie App. aux Arts.*)

The strength and goodness of gunpowder is most accurately determined by measuring its actual projectile force by the *éprouvette*, which is a small strong barrel in which a given quantity of it is fired, and the force of expansion measured by the action exerted on a strong spring or a great weight. Another method is, to fire a heavy ball from a short mortar, with a given weight of the powder, and to find the range of projection. The *éprouvette* formerly used in France, was a mortar seven inches (French) in calibre, which, with three ounces of powder, should throw a copper globe of 60 lbs. weight to the distance of 300 feet. Gunpowder is sometimes tried by placing two heaps of about sixty grains each upon clean writing-paper, three or four inches asunder, and firing one of them by a red-hot wire: if the flame ascends quickly with a good report, sending up a ring of white smoke, leaving the paper free from white specks and not burnt into holes, and if no sparks fly off from it so as to set fire to the contiguous heap, the powder is very good; if otherwise, the ingredients are badly mixed or impure. It appears from Count Rumford's experiments on the force of gunpowder (*Phil. Trans.*, LXXXVII. 254), that 28 grains, confined in a cylindrical space which it just filled, tore asunder a piece of iron which would have resisted a strain of 400,000 lbs. (See also a report in M. PROBERT'S *Memoir on Gunpowder*; *Ann. de Ch. et Ph.*, LXII. 250.)

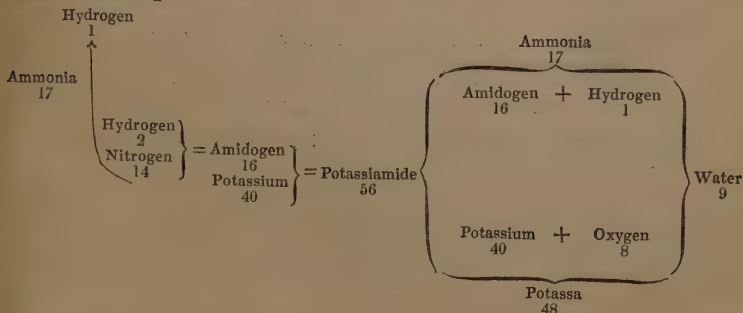
Gunpowder may, it is said, be inflamed by a violent blow; if mixed with powdered glass, or any other harder substance, and struck with a heavy hammer upon an anvil, it almost always explodes. It readily burns under water, and by using a slowly burning powder, such as squibs are filled with, inflamed in a tube of copper, the gaseous products may be collected over water in the pneumatic trough. The portfires used by the artillery also answer very well for this experiment.

Analysis of Gunpowder.—To analyze this compound, boil it with four parts of water, edulcorate the residue, dry it at 212° , and weigh; the loss indicates the nitre. The dry residue, composed of charcoal and sulphur, may be decomposed by spreading it upon an earthen plate, and burning off the sulphur at the lowest possible heat; the charcoal will remain, still however retaining a little sulphur. A more accurate process consists in introducing the mixture into a small retort furnished with a stop-cock, exhausted, and filled with chlorine; heat applied volatilizes the chloride

of sulphur and leaves the charcoal, which may be washed, dried, and weighed. Another mode of analyzing gunpowder consists in separating the nitre by water, evaporating to dryness, and fusing the salt. To obtain the sulphur, 5 grains of the powder, 5 of carbonate of potassa, 5 of nitre, and 20 of pure common salt, are to be intimately mixed, and placed on the fire in a platinum vessel; the sulphur is slowly acidified, and when the mass becomes white it is dissolved in water, saturated with nitric or hydrochloric acid, and solution of chloride of barium added, so long as it occasions a precipitate; the sulphate of baryta thrown down is then collected, washed, and ignited, and its weight indicates the quantity of sulphur contained in the gunpowder by the usual computation. (GAY LUSSAC, *Ann. de Ch. et Ph.*, xvi. 437.) Sometimes after the separation of the nitre by water, the residuary sulphur and charcoal are dried, and the relative proportion of the latter determined by ignition with oxide of copper, as in organic analyses.

ACTION OF POTASSIUM ON AMMONIA. POTASSIAMIDE.—The action of potassium on gaseous ammonia was first examined by Gay Lussac and Thenard, and by Sir H. Davy. When potassium is heated in ammonia, hydrogen is evolved, and a fusible olive-coloured substance is obtained, of a crystalline fracture, translucent at the edges, heavier than water, and a non-conductor of electricity. It fuses at a little above 212° . It burns in oxygen, producing hydrated potassa and nitrogen: exposed to air, it slowly deliquesces, and evolves ammonia: water rapidly acts upon it, producing potassa and ammonia. The volume of hydrogen evolved by the action of potassium on ammonia is the same as that which it would have evolved from water; so that when 1 atom of potassium acts on 1 of ammonia, 1 of hydrogen is evolved, and the remaining elements of the ammonia, (namely 1 atom of nitrogen, and 2 of hydrogen,) combine with the potassium; now 1 of nitrogen and 2 of hydrogen constitute amidogen; hence this resulting compound has been termed *potassiamide*, its formula being $(po + n + 2h)$.

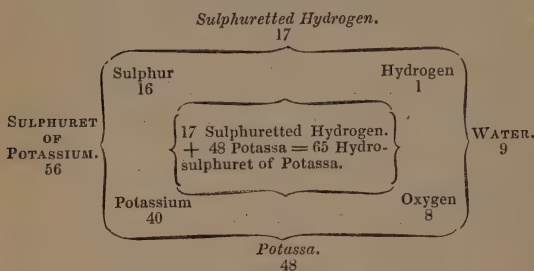
The following diagram, to which the equivalent numbers are attached, shows that ammonia, acted upon by potassium, loses one equivalent of hydrogen, and forms potassiamide; and that potassiamide and water yield ammonia and potassa:—



POTASSIUM AND SULPHUR. SULPHURETS OF POTASSIUM.—When potassium and sulphur are heated together in an exhausted tube, the sulphur

not being in excess, intense action ensues, attended by the vivid combustion of the potassium, and a brownish-gray compound results: when proper proportions of the materials are used, this is *protosulphuret of potassium* ($po + s$). The same compound is obtained by heating atomic proportions of sulphate of potassa and charcoal (lamp-black), in which case, especially if there be excess of lamp-black, the product is pyrophoric. Protosulphuret of potassium is also formed by passing hydrogen through a red-hot tube containing sulphate of potassa: water is formed in consequence of the deoxidizement, by the hydrogen, of the acid and of the potassa. Thus procured it is a dark reddish-brown deliquescent substance, fusible at a heat below redness, of a caustic and sulphureous taste, soluble in water and alcohol, and when heated by the blowpipe, becomes incrustated with sulphate of potassa. From the mode of forming this compound it obviously consists of

Potassium	1	. .	40	. .	71.4
Sulphur	1	. .	16	. .	28.6
<hr/>						
Protosulphuret of potassium	1			56		100.0



When sulphuret of potassium is put into water, it is generally assumed that it yields a solution of *hydrosulphuret of potassa* ($po + o$) + ($h + s$), in consequence of the decomposition of one proportional of water, by one of the sulphu-

ret, as shown in the annexed diagram: but Berzelius does not admit the decomposition of water in these cases, but considers the solution as containing the undecomposed sulphuret.

A similar compound may be obtained by passing sulphuretted hydrogen through an aqueous solution of potassa, and if this be carefully evaporated in a retort so as to exclude air, it forms colourless prismatic crystals; which, independent of water of crystallization, are considered as containing

Potassa	1	. .	48	. .	73.85
Sulphuretted hydrogen	1	. .	17	. .	26.15
<hr/>						
Hydrosulphate of potassa	1			65		100.00

HYDROSULPHURET OF POTASSIUM. ($po + h + 2s$).—When potassium is heated in sulphuretted hydrogen gas it burns, and the gas diminishes in volume. During this action the potassium decomposes one proportional of the gas, evolves hydrogen, and combines with its sulphur to form sulphuret of potassium, which, uniting without decomposition with another proportional of the gas, forms a compound of

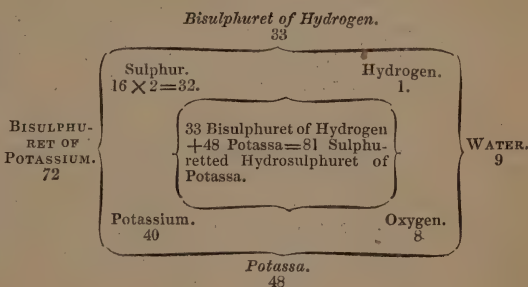
Sulphuret of potassium	1	. .	56	. .	76.71
Sulphuretted hydrogen	1	. .	17	. .	23.29
<hr/>						
Hydrosulphuret of potassium	1			73		100.00

It is to such compounds that the term *sulphur salts* properly applies. This hydrosulphuret yields with water a colourless solution of bihydrosulphuret of potassa ($po + o$) + $2(h + s)$. With dilute acids it evolves two volumes of sulphuretted hydrogen. When dilute acids are dropped into a solution of this hydrosulphuret, one volume of sulphuretted hydrogen is evolved, and no sulphur precipitated: when the solution is exposed to air, it absorbs oxygen, and becomes converted into hyposulphite of potassa.

BISULPHURET OF POTASSIUM. ($po + 2s$).—When 4 parts of potassium are heated with 3 of sulphur, a brown fusible crystalline substance is obtained, permanent at a red heat, and consisting of

Potassium	1	. .	40	. .	55.6
Sulphur	2	. .	32	. .	44.4
		<hr/>		<hr/>		
Bisulphuret of potassium		1		72		100.0

Acting upon water this compound decomposes one proportional of that fluid, and forms a yellow solution of sulphuretted hydrosulphuret of potassa, or of a compound of potassa with bisulphuretted hydrogen ($po + o$) + $(2s + h)$ as in the annexed diagram.



The solution therefore contains

Potassa	1	. .	48	. .	59.3
Bisulphuret of hydrogen		1	. .	33	. .	40.7
		<hr/>		<hr/>		
		1		81		100.0

When the dilute acids are added to this aqueous solution, sulphuretted hydrogen is evolved and sulphur precipitated in a peculiar white state, hydrated according to Thomson, but containing, according to Rose, a little bisulphuretted hydrogen; but if a *strong* solution of it be poured into hydrochloric acid, a viscid substance falls, which is bisulphuretted hydrogen (see page 481). Exposed to air, this solution passes into a hyposulphite, and sulphur is deposited.

It appears that the above are the only two definite compounds of sulphur and potassium; they are both permanent at high temperatures; but these unite indefinitely with sulphur by fusion at a moderate heat. Berzelius describes seven sulphurets of potassium, in which one proportional of metal is combined respectively with 1, 2, 3, $3\frac{1}{2}$, 4, $4\frac{1}{2}$, and 5 proportionals of sulphur (*Ann. Phil., N.S.*, iv. 214), but the definite nature of these compounds seems open to some doubt.

POTASSA AND SULPHUR.—When sulphur is fused with hydrate of potassa, the water of the hydrate evaporates, and the oxide of potassium is decomposed, giving rise, at a red heat, to sulphuret or bisulphuret of potassium (according to the quantity of sulphur used), and to hyposulphite (which becomes sulphate) of potassa. It does not appear that any sulphurous acid is in these cases evolved.

When anhydrous carbonate of potassa mixed with half its weight of sulphur is kept at a low red heat till carbonic acid ceases to be evolved, the result, according to Berzelius, is a *tersulphuret of potassium* ($po + 3s$) mixed with sulphate of potassa; the elements concerned in the product are 4 atoms of potassa and 10 of sulphur, which yield 3 atoms of tersulphuret of potassium, and 1 of sulphate of potassa; or in symbols, $4(po + o) + 10s = 3(po + 3s)$ and $(po + o) + (s + 3o)$.

The *potassii sulphuretum* of the Pharmacopœia is a similar compound of sulphuret of potassium and sulphate of potassa, obtained by heating 1 part of sulphur and 3 of carbonate of potassa; or, according to Phillips, (*Translation of Pharmacopœia*,) 4 atoms of carbonate of potassa, heated with 4 of sulphur, yield 1 atom of sulphate of potassa and 3 of sulphuret of potassium, 4 atoms of carbonic acid being expelled; as in the following equation:— $4(po + o + car') + 4s = 3(po + s) + (po + o) + (s + 3o)$.

The compounds obtained by fusing potassa, or its carbonate, with sulphur, were formerly designated *Livers of Sulphur*, in consequence of their colour; and the conversion of sulphate of potassa into liver of sulphur by the action of charcoal and heat, was an experiment instituted by Stahl in support of the phlogistic hypothesis. Exposed to air, these sulphurets deliquesce, and exhale a disagreeable smell; their taste is bitter, acrid, and nauseous. The general results of dissolving them in water have been above noticed.

When sulphur is boiled with the hydrosulphuret, or when excess of sulphur is boiled in solution of potassa, bihydrosulphuret of potassa may be obtained; but as this compound, when in solution, dissolves variable and apparently indefinite portions of sulphur, an uniform combination is not in this way easily obtainable.

HYPOSULPHITE OF POTASSA ($po + o$) + ($2s + 2o$) or ($P + \bar{s}$) is formed by decomposing hydrosulphuret of potassa by sulphurous acid, and evaporating to a pellicle, when it forms acicular crystals, of a cooling bitter taste, and deliquescent. After careful drying, it takes fire upon elevating the temperature, and burns like tinder. Its solution readily dissolves moist chloride of silver; and when exposed to air becomes sulphite, and ultimately sulphate, of potassa. This salt is also formed when the alcoholic solution of sulphuret of potassium is exposed to air, and the adhering sulphuret washed from its crystals by alcohol: or by boiling a solution of sulphite of potassa with sulphur.

SULPHITE OF POTASSA ($P + \bar{s}$) is formed by passing sulphurous acid into a solution of potassa, or of its carbonate, and evaporating out of the contact of air. Rhomboidal plates or prisms, or sometimes acicular tufts, are obtained, white, anhydrous, of a sulphurous taste, and soluble in about their weight of water. By exposure to air, they pass into sulphate

of potassa. Berzelius observes that there is a *bisulphite of potassa*, more easily crystallizable than the sulphite, and generally confounded with it.

Sulphite of potassa consists of

Potassa	1	48	60
Sulphurous acid	1	32	40
<hr/>			
Sulphite of potassa	1	80	100

HYPOSULPHATE OF POTASSA ($po + o$) + ($2s + 5o$) or $P + s'$ is obtained by decomposing a solution of hyposulphate of baryta, by sulphate of potassa. It forms permanent crystals of a bitter taste, difficultly soluble in cold, but readily so in hot water. It is anhydrous. Its crystals are described by Mr. Levy in the *Quarterly Journal*, xv. 285. It consists, according to Heeren (*Ann. de Ch. et Ph.*, xl. 30), of

Potassa	1	48	40
Hypsulphuric acid	1	72	60
<hr/>			
Hypsulphate of potassa	1	120	100

SULPHATE OF POTASSA. ($po + o$) + ($s + 3o$), or $(P + s')$, or $\ddot{K} \ddot{S}$.—This salt is the result of several chemical operations carried on upon a large scale in the processes of the arts. It may be formed directly by saturating diluted sulphuric acid by carbonate of potassa. It is the *sal de duobus* and *arcanum duplicatum* of the old chemists: the *potassæ sulphas* of the *London Pharmacopæia*. Its taste is bitter and saline. It generally crystallizes in short six-sided prisms, terminated by six-sided pyramids. The body of the prism is often wanting, and the triangular-faced dodecaëdron results. These forms have been described by Levy (*Quarterly Journal*, xv. 285), they result, according to Phillips (*Trans. Pharm.*), from a primary right rhombic prism. According to Mitscherlich its primitive form is a rhombic octoëdron, and it is isomorphous with seleniate, and also with chromate of potassa. The crystals, whilst forming, sometimes emit a yellow light. They are anhydrous. This salt dissolves in 16 parts of cold, and 5 of boiling water; or, according to Gay Lussac, 100 parts of water at 32° dissolve 8.36 of this salt, and for each degree above 32° , it takes up 0.1741 parts in addition; in consequence of its difficult solubility, it is thrown down, in a white granular powder, when sulphuric acid is added to a moderately strong solution of potassa. It is insoluble in alcohol. Exposed to a red heat, it decrepitates and melts, but is not decomposed. At very high temperatures it is volatilized. It is decomposed at a red heat by hydrogen, which carries away the oxygen both of the acid and of the potassa, and converts it into sulphuret of potassium. When fused with sulphur, this salt undergoes no change; the sulphur sublimes unaltered. (VAUQUELIN, *Ann. de Ch. et Ph.*, v. 20.) Intensely heated with one-fifth its weight of powdered charcoal, it produces sulphuret of potassium. When about 2 parts of sulphate of potassa and 1 of lamp-black, intimately mixed in fine powder, are heated to redness in a coated phial, and great care taken to exclude the air during cooling, a compound is obtained which takes fire upon exposure to air. It appears to contain a compound of potassium, which powerfully attracts oxygen, and thus evolves heat enough to inflame the charcoal and sul-

phur. Gay Lussac attributes the combustibility of common pyrophorus (see ALUMINA) to the presence of this compound.

Sulphate of potassa consists of

Sulphate of potassa consists of				Kirwan.	Dalton.
Potassa	1	48	54.5	55	55.3
Sulphuric acid	1	40	45.5	45	44.7
<hr/>					
Sulphate of potassa	1	88	100.0	100	100.0

BISULPHATE OR SUPERSULPHATE OF POTASSA, $(po + o) + 2(s + 3o)$ or $(P + 2S')$ or $K S_2$, is formed by adding sulphuric acid to a hot solution of sulphate of potassa; or by boiling sulphate of potassa with half its weight of sulphuric acid in a platinum crucible, till none of the acid escapes when the heat approaches redness: the saline mass, dissolved and evaporated, furnishes crystals which affect various forms dependent upon the circumstances under which they are obtained: sometimes they present an acicular mass; at other times they are tabular; and sometimes flattened prisms.

According to Geiger they consist of

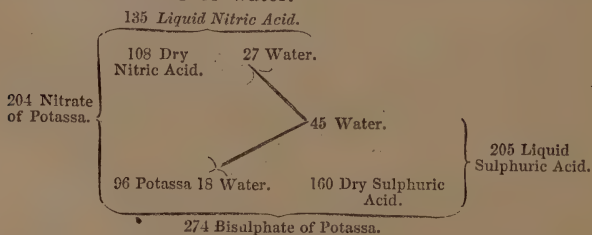
According to Geiger they consist of				Acicular.	Prismatic.
Potassa	1	48	32.9	33.83	32.53
Sulphuric acid	2	80	54.8	55.43	54.77
Water	2	18	12.3	10.74	12.70
<hr/>					
Crystallized bisulphate of potassa	1	146	100.0	100.00	100.00

The crystals of bisulphate of potassa are soluble in about half their weight of boiling water, and twice their weight of water at 40° . When dissolved in a large quantity of water and evaporated, crystals of sulphate of potash are deposited from a sour mother-liquor.

By a continued red heat this salt loses its excess of acid. Alcohol added to its aqueous solution throws down neutral sulphate of potassa.

Bisulphate of potassa is also formed in the distillation of equal weights of nitre and sulphuric acid: nitric acid passes over, and a residuary bisulphate of potassa is produced, commonly known under the name of *sal enixum**. It is the *arcanum duplicatum*, or *panacea Holsatica* of old pharmacutists. It is used as a substitute for dilute sulphuric acid for cleansing coin and other works in metal; and has a place in some *Pharmacopœia*.

Mr. Phillips gives the following diagram illustrating the formation of crystallized bisulphate of potassa by the mutual action of 2 atoms of nitrate of potassa and 4 atoms of liquid sulphuric acid; but he assumes that in these 4 atoms of acid there are 5 of water, and that 2 atoms of liquid nitric acid contain 3 of water.



* This salt, from the variable quantity of nitric acid, is generally a mixture of sulphuric acid used in the distillation of sulphate and bisulphate of potassa.

According to Jacquelin (*Ann. de Ch. et Ph.*, LXX. 311) an *anhydrous bisulphate* of potassa is obtained when 1 equivalent of sulphate of potassa and not less than $1\frac{1}{2}$ equivalents of liquid sulphuric acid are dissolved together in water and the solution evaporated; it yields prismatic needles, which when left in the mother-liquor gradually disappear, and rhomboëdrons of hydrated bisulphate are formed. The anhydrous salt may be dissolved and recrystallized from a quantity of hot water merely sufficient for its solution, but is decomposed by a larger quantity of water.

SESQUISULPHATE OF POTASSA. ($P + 1\frac{1}{2}S'$).—This salt has been described and analyzed by Mr. Phillips (*Phil. Mag.*, N.S., ii. 420); he obtained it as the residue of the distillation of equal weights of nitre and sulphuric acid (sp. gr. 1·8442). It was in filamentous crystals, and consisted of

Potassa	2	96	42·67
Sulphuric acid	3	120	53·33
Water	1	9	4·00
<hr/>			
Crystallized sesquisulphate of potassa 1		225	100·00

AMMONIO-SULPHATE OF POTASSA ($P + A + 2S'$) is obtained by adding ammonia to bisulphate of potassa, or by mixing solutions of sulphate of ammonia and sulphate of potassa, and setting aside to crystallize: it forms transparent prisms of a bitter taste: 100 of water at 60° dissolve 13. (LINK, CRELL'S *Annals*, 1796.) It consists of

Sulphate of potassa	1	88	48·6
Sulphate of ammonia	1	57	31·5
Water	4	36	19·9
<hr/>			
Crystallized ammonio-sulphate of potassa 1		181	100·0

PHOSPHURET OF POTASSIUM is a chocolate-brown compound, which rapidly decomposes water, evolving phosphuretted hydrogen gas. It is formed by cautiously heating atomic equivalents of potassium and phosphorus out of the contact of air; or by decomposing phosphuretted hydrogen by potassium, which, when heated in that gas, forms this phosphuret and evolves pure hydrogen. The composition of this phosphuret has not been accurately determined, but it is probably a protophosphuret. When heated with potassium it appears capable of combining with an additional proportion of that substance, and forms a lead-coloured compound, in which it is probable that 2 proportionals of potassium are combined with 1 of phosphorus. When these phosphurets are put into water, potassa, hypophosphite of potassa, hydrogen, and phosphuretted hydrogen, are the results.

By heating potassium with glacial phosphoric acid, Gay Lussac and Thenard obtained a brown compound which decomposed water: it was probably a mixture of phosphuret of potassium and phosphate of potassa.

HYPOPHOSPHITE OF POTASSA ($po + o$) + ($2p + o$) or ($P + \bar{p}$) has been examined by Dulong. It is very deliquescent, and soluble in water and alcohol nearly in all proportions. When heated it evolves phosphuretted hydrogen and phosphorus, and is converted into phosphate of potassa.

(*Ann. de Ch. et Ph.*, ii. 142.) It is best prepared by mixing a solution of hypophosphite of lime with one of carbonate of potassa, filtering, and evaporating to dryness: alcohol, digested upon the residue, takes up the hypophosphite of potassa: it is uncrystallizable, but may be dried in vacuo. (ROSE, *Quarterly Journal*, iv. 206.) The substance described by Grotthus (*Ann. de Chim.*, lxiv. 20), as resulting from the action of phosphorus upon a solution of potassa, is probably this hypophosphite.

PHOSPHITE OF POTASSA ($po + o$) + ($p + 1\frac{1}{2}o$) or ($P + p$) is a soluble deliquescent uncrystallizable salt, insoluble in alcohol. (DULONG.) When heated, hydrogen is evolved and a neutral phosphate remains.

PHOSPHATE OF POTASSA ($po + o$) + ($p + 2\frac{1}{2}o$) or ($P + p'$) or K_2, P_2O_5 , is a soluble difficultly-crystallizable salt, of a cooling, urinous taste, formed by adding carbonate of potassa to hot phosphoric acid till the solution ceases to affect vegetable blues. It is insoluble in alcohol. It may be obtained by very careful evaporation, in four-sided prisms, and octoëdrons, composed, according to Thomson, of

Potassa	1	48	51·6
Phosphoric acid	1	36	38·7
Water	1	9	9·7
<hr/>			
Crystallized phosphate of potassa	1	93	100·0

DIPHOSPHATE OF POTASSA ($2P + p'$) is formed by adding hydrate of potassa to the *phosphate*, and removing the excess of alkali by alcohol, when the basic salt (diphosphate) falls in the form of an oily liquid. (BERZELIUS.) It may also be obtained by adding hydrate of potassa to a solution of the phosphate, *evaporating to dryness*, and then removing the excess of potassa by alcohol: it is tasteless, insoluble in cold water, but soluble in hot water, and precipitates as the solution cools, in the form of a gritty powder: it is extremely fusible: it is soluble in nitric, hydrochloric, and phosphoric acids, and the solutions are glutinous; when sufficiently diluted, the alkalis occasion no precipitate in these solutions. (THOMSON.) It consists of

Potassa	2	96	72·73
Phosphoric acid	1	36	27·27
<hr/>			
Diphosphate of potassa	1	132	100·00

BIPHOSPHATE OF POTASSA ($P + 2p'$) is formed by dissolving the neutral phosphate in phosphoric acid, and evaporating till crystals are obtained, which are prismatic and very soluble in water, but insoluble in alcohol; at a high temperature it fuses into a transparent glass. According to Mitscherlich (*Ann. de Ch. et Ph.*, xix. 364), the biphosphate of potassa consists of

				Mitscherlich.
Potassa	1	48	34·8	34·40
Phosphoric acid	2	72	52·2	52·48
Water	2	18	13·0	13·12
<hr/>				
Crystallized biphosphate of potassa	1	138	100·0	100·00

POTASSIUM AND SELENIUM. ($po + se$).—When these substances are heated together, they combine with intense action, and produce a gray crystalline compound, forming a deep-brown solution with water, from which acids evolve seleniuretted hydrogen and precipitate selenium. When selenium is heated with excess of potassium, an explosion ensues, and a compound is obtained which furnishes a red solution, and evolves hydrogen by the action of water. The odour and general characters of these compounds so much resemble those with sulphur, as not easily to be distinguished except by the brown and red colours of their solutions.

When powdered selenium is boiled in solution of potassa, a dark-brown solution of an hepatic taste and smell is the result, from which acids precipitate selenium. Fused with potassa, selenium produces seleniate of potassa and seleniuret of potassium.

POTASSA AND SELENIOUS ACID form, according to Berzelius, a neutral *selenite of potassa* ($po + o$) + ($se + 2o$) or ($P + \overline{se}$), a *biselenite* ($P + 2\overline{se}$), and a *quadriselenite* ($P + 4\overline{se}$). The first is difficultly crystallizable, somewhat deliquescent, and insoluble in alcohol. The second forms plumose crystals, very sparingly soluble in alcohol. The third is uncrystallizable. (*Ann. de Ch. et Ph.*, ix. 257.)

SELENATE OF POTASSA. ($po + o$) + ($se + 3o$) or ($P + se'$).—This salt may be obtained by fusing nitre with selenium or selenious acid, or by saturating the selenic acid by potassa. From the statement of Mitscherlich it consists of

Potassa	1	48	42.9
Selenic acid	1	64	57.1
<hr/>			
Seleniate of potassa	1	112	100.0

According to the same authority, the seleniates and the sulphates are isomorphous. (*Ann. de Ch. et Ph.*, xxxvi. 104.)

POTASSIUM AND CARBON.—When potassa is decomposed at high temperatures by carbon, a black substance remains in the retort, which is probably a *carburet of potassium*. ($po + car$.) It takes fire upon water; and if plunged into that fluid evolves carburetted hydrogen. It is probable that several of the pyrophoric charcoals contain potassium.

POTASSA AND CARBONIC ACID.—These bodies combine in two proportions, forming the *carbonate* and the *bicarbonate* of potassa, compounds which have been long used and known under various names; such as *fixed nitre*, *salt of tartar*, *salt of wormwood*, *vegetable alkali*, &c. Their composition was first ascertained by Black. Bergman, in 1774, described their most essential properties. (*Opuscula*, vol. i., p. 13.)

CARBONATE OF POTASSA ($po + o$) + ($car + 2o$) or $P + car'$ or $\dot{K} \ddot{C}$, is a salt of great importance in many arts and manufactures, and is known in commerce in different states of purity, under the names of *wood-ash*, *pot-ash*, *pearl-ash*, and *subcarbonate of potassa*.

It may be obtained directly, by passing carbonic acid into a solution

of potassa, till saturated, evaporating to dryness, and exposing the dry mass to a red-heat; or indirectly, by burning purified *tartar* (bitartrate of potassa), lixiviating the residue, and evaporating to dryness, whence the name *salt of tartar* has been applied to it. A mixture of purified tartar and nitre projected into a crucible heated to dull redness, also affords by its combustion a residue of carbonate of potassa, which may be obtained by lixiviation as the preceding.

Carbonate of potassa is fusible without decomposition, at a red-heat; its specific gravity is 2·6; it is very soluble in water, which at 55° takes up about its own weight; it deliquesces by exposure to air, forming a dense solution, once called *oil of tartar per deliquium*. Its taste is alkaline, and it renders vegetable blues green. It consists, in its fused or anhydrous state, of

				Vauquelin.	Dalton.
Potassa	1	48	68·6	67	68·9
Carbonic acid	1	22	31·4	33	31·1
Carbonate of potassa	1	70	100·0	100	100·0

A saturated solution of carbonate of potassa in water contains about 48 per cent. of the salt, and has a specific gravity of 1·5. The following table, showing the quantity of dry carbonate of potassa in solutions of different specific gravities, is by Richter. (Gmelin, i., 2 abt., p. 530, Ed. 1827.)

S. G.	Per Cent.	S. G.	Per Cent.	S. G.	Per Cent.
1·58 . . .	37·4	1·33 . . .	27·0	1·18 . . .	13·5
1·56 . . .	36·5	1·36 . . .	26·0	1·16 . . .	12·0
1·54 . . .	35·4	1·34 . . .	24·5	1·14 . . .	10·6
1·52 . . .	34·1	1·32 . . .	22·7	1·12 . . .	9·4
1·50 . . .	32·7	1·30 . . .	20·8	1·10 . . .	8·2
1·48 . . .	31·8	1·28 . . .	19·7	1·08 . . .	6·6
1·46 . . .	30·9	1·26 . . .	18·7	1·06 . . .	4·9
1·44 . . .	29·9	1·24 . . .	17·5	1·04 . . .	3·3
1·42 . . .	29·0	1·22 . . .	16·3	1·02 . . .	1·7
1·40 . . .	28·0	1·20 . . .	15·1		

If a solution of this carbonate be evaporated till of a specific gravity of 1·62 whilst warm, and then poured into a tall cylindrical glass vessel, and suffered slowly to cool, it furnishes crystals in long rhomboidal tables, which are very deliquescent. The remaining mother-liquor, when cold, yields further crystals on evaporation, or when long kept; in the latter case, the crystals are rhombic octoëdra. (BERARD, *Ann. de Ch. et Ph.*, LXXI. 50. GIESE, *Scherer's Annalen*, iv. 294.) Fabbroni afterwards described these crystals, without being aware that they were previously known (*Ann. de Ch. et Ph.*, xxv. 5). They consist of

				Giese.	Berard.
Potassa	1	48	54·5	55	79·4
Carbonic acid	1	22	25·0	25	
Water	2	18	20·5	20	20·6
Crystallized carbonate of potassa	1	88	100·0	100	100·0

Carbonate of potassa is insoluble in alcohol, and is occasionally employed to deprive alcohol of water. Berzelius states, that if steam be passed over this salt in a red-hot tube, its carbonic acid is expelled, and

hydrated potassa formed. A few of the metals, and charcoal at very high temperatures, decompose it with the production of potassium. The action of sulphur and of phosphorus upon this carbonate has already been noticed.

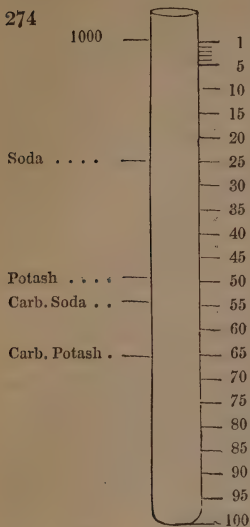
MANUFACTURE OF POTASH AND PEARLASH. ALKALIMETRY.—The great consumption of carbonate of potassa in various manufactures is exclusively supplied by the combustion of vegetables, and consequently its production is almost limited to those countries which require clearing of timber, or where there are vast natural forests. The English market is chiefly supplied from North America. If any vegetable growing in a soil not impregnated with sea-salt be burned, the residue, which is in the form of a brown saline mass, contains a large relative proportion of carbonate of potassa, and is commonly called *rough*, or *crude potash*. If it be again calcined so as to burn away the carbonaceous matter entirely, it becomes a white mass, generally termed *pearlash*.

The pearlash of commerce contains a variety of impurities (especially chloride of potassium and sulphate of potassa), which render it of variable value. In general, its purity may be judged of by its easy solubility in water, two parts of which should entirely and easily dissolve one part of the salt without the aid of heat; the residue, if any, consists of impurities. The quantity of nitric acid of a given density, requisite to saturate a given weight, may also be resorted to as a criterion of its purity. 100 parts of nitric acid, specific gravity 1.36, will saturate 65.7 parts of dry carbonate of potassa, which are equivalent to 45 parts of pure potassa; or, 355 grains of diluted sulphuric acid of the specific gravity 1.141 exactly neutralize 100 grains of pure carbonate of potassa. Hence, if we dissolve 100 grains of the alkali to be examined, in six or eight parts of water, and gradually add the test sulphuric acid till we find, by the application of violet or mallow paper, that the alkali is exactly neutralized, we may deduce, from the weight of the acid consumed, the proportion of real carbonate present: for as 355 is to 100, so is the weight of the test-acid employed to that of the pure carbonated alkali present. To save trouble, the acid properly diluted may be put into a glass tube, so graduated as to show directly the value of the alkali by the quantity consumed in its saturation. Thus we find, by reference to the scale of equivalents, that 100 parts of carbonate of potassa are saturated by 70 of sulphuric acid, specific gravity 1.85. If, therefore, we put 70 grains of such acid into a tube divided into 100 parts, and fill it up with water, it follows that the quantity of carbonate of potassa existing in any sample of pearlash under examination, will be directly shown by the measure of such diluted acid required for saturation; 100 grains of the sample, if pure carbonate, would require the whole 100 measures of acid: but if only containing 50 *per cent.* of pure carbonate, the 100 grains would be saturated by 50 measures of the test-acid, and so on. Such graduated tubes are sometimes called *alkalimeters*.

The following directions respecting their construction and use, I abstract from Mr. FARADAY'S *Manipulation*. Let a tube, closed at one end (fig. 274), of about three-fourths of an inch internal diameter, and nine inches and a half in length, have 1000 grains of water weighed into it; then let the space it occupies be graduated into 100 equal parts,

and every ten divisions numbered from above downwards. At 23.44 parts, or 76.56 parts from the bottom, make an extra line a little on one side, or even on the opposite side to the graduation, and write at it with

a scratching diamond *soda*; lower down at 48.96 parts, make another line and write *potash*; still lower at 54.63 parts, a third line marked *carb. soda*; and at 65 parts a fourth, marked *carb. potash*. It will be observed that portions are measured off, beneath these marks, in the inverse order of the equivalent numbers of these substances, and consequently directly proportionate to the quantities of any particular acid, which will neutralize equal weights of the alkalis or their carbonates. As these points are of great importance, it will be proper to verify them by weighing into the tube first 350, then 453.7, then 510.4, and lastly 765.6 grains of water, which will correspond with the marks if they are correct. Or the graduation may be laid down from the surface of the four portions of fluid when weighed in, without reference to where they fall upon the general scale. The tube is now completed, except that it should be observed whether the aperture can be perfectly and securely covered by the thumb of the left



hand, and if not, or if there be reason to think it not ultimately secure, then it should be heated and contracted until sufficiently small.

Diluted sulphuric acid must now be prepared to be used with the tube. When of a specific gravity of 1.1268, it will be very nearly, if not accurately, of the strength required; and this may be obtained by mixing one part by weight of oil of vitriol of specific gravity 1.82, with four parts of water. If, when cold, the specific gravity of this diluted acid be as above mentioned 1.1268, it must be nearly, if not exactly, of the strength required; but before being admitted into use, should be examined experimentally. Assuming it, however, as being absolutely correct, it will be found that a quantity measured into the tube up to any one of the four marks described, is sufficient to neutralize 100 grains of the dry alkali or carbonate set down at the mark; consequently, if water be added in the tube, thus filled up to any one of the marks, until the 100 parts are full, and the whole uniformly mixed, one part of such diluted acid will neutralize one grain of the alkali or carbonate named at the mark, up to which the tube was first filled with the acid of specific gravity 1.1268.

When a specimen of potash, barilla, or kelp, is to be examined by this instrument, 100 grains are to be weighed out, dissolved in warm water, filtered, the insoluble portion washed, and the solution added to the rest; by this process the alkali will be separated from carbonate of lime, or other insoluble matters, which otherwise might cause errors in the estimation. The alkaline solution is to be put into a basin on the sand-bath, and then the tube and acid prepared. For this purpose some

of the acid, of specific gravity 1.1268, is to be poured into the tube until it rises up to the mark indicating the substance to be tested for; *potash* or *carbonate of potash* for the potash or pearlash of commerce, and *soda* or *carbonate of soda* for barilla or kelp: then water is to be added carefully, until the hundred parts are filled, and closing the tube with the finger, its contents are to be perfectly agitated and mixed.

The alkali in the basin is now to be neutralized with the acid in the tube. After having once placed the thumb of the left hand over the aperture of the tube, it is not to be again removed; but inverting the tube by turning the hand so that the thumb and the mouth of the tube are downwards, the acid is to be let out gradually into the alkaline solution, by relaxing the thumb and admitting a succession of small bubbles of air; the hot solution beneath is to be continually stirred, so as to mix the acid instantly with the whole, and the operator must proceed with increased caution as the point of neutralization is approached. Very small quantities of the acid may be added, by slightly relaxing the thumb so as to permit a minute quantity, less than a drop, to flow to its extremity, and touching it with the glass rod; the final adjustment may thus be made more accurately, than by dropping the acid from the lip of the tube. The process must be carried on until the alkali is found by the test-papers to have been exactly neutralized: then the tube must be inverted, the thumb removed, drawing its under surface over the edge of the tube, so as to leave as much as possible of the fluid that otherwise might adhere to it, and having allowed the sides to drain, it must be observed how many parts of acid have been used, the number of which will indicate the number of grains of the alkali or carbonate, contained in the 100 grains of the impure alkali operated with*.

With respect to the proper strength of the acid, it is to be examined in the following manner: crystals of bicarbonate of potash are to be fused in a platina crucible, the fluid poured out upon a clean, cold metal plate, and a piece of the resulting solid, estimated to be 70, 80, or 100 grains, weighed in water; in this way a known weight of pure carbonate of potash will be obtained in solution. The solution is then to be diluted, heated, and neutralized by acid from the tube diluted as before described, from the mark of carbonate of potash. If it be found that as many parts of the acid have been used as of grains of the carbonate weighed out, the acid is of proper strength: if more acid has been used, it is too weak; if less has been sufficient, it is too strong. Suppose for instance that 100 grains of the salt (fused carbonate of potash) had been used, and that 90 parts of the acid were sufficient; then these 90 parts ought to have occupied the 100, and consequently the 100 parts contain one-tenth too much acid, in consequence of the experimental acid itself containing one-tenth more than it ought to do. Hence the latter must be diluted with such a

* Some of the impure sources of potash and soda used in the arts, contain amongst other substances sulphuret and sulphite of alkali. Both these occasion errors in the mode of estimation above described, to obviate which MM. Welter and Gay Lussac (*Annales de Chimie*, xiii. 212) advise, that after the soluble parts have been separated by water, a little chlorate of potash should be added to them, the whole evaporated and heated to redness. This converts the sulphuret and sulphite into neutral sulphate, and then upon re-dissolving the whole, the caustic and carbonated alkali may be ascertained as above described.

quantity of water as will make nine volumes into ten, or by one-ninth its volume; for as the 90 parts used are to the 100 parts they ought to have occupied, so is any number of parts by volume of the acid under trial, to the number of parts which it ought to occupy. The difference between the two last numbers will give the quantity of water in volumes, to be added to the acid expressed by the first of them, in order to correct it and make it of proper strength. On the contrary, if it were found that the 100 parts were insufficient, and that 10 parts more of similar acid were required, then there is too much water by one-eleventh of the whole in bulk, the correction for which would be one-tenth more of the 35 parts of acid put into the tube up to the mark 65 *carb. potassa*. This tenth is 3.5 parts, but as only a fifth of that or 0.7 parts is acid, therefore 0.7 parts by weight of the same oil of vitriol that was used before must be added for every 35 parts of the mixed acid. The correction in any other case may be easily made, by considering that the number of parts over a hundred which are necessary to saturate the 100 grains of carbonate of potash, are proportionate to the quantity of oil of vitriol which must be added to bring the experimental acid to proper strength: thus if 136 parts of the diluted acid were used, then thirty-six-hundredths more of the weight of oil of vitriol already used must be added; and the quantity of oil of vitriol that was added at first being known to be one-fifth by weight, the additional quantity required is easily ascertained. These corrections are not strictly accurate, but sufficiently so to meet even the exaggerated cases put of a difference of 10 parts, and to bring it within the limit of errors of experiment.

Sometimes instead of using test-papers, a little of the neutralized blue-cabbage liquor, or of infusion of litmus, may be put into the alkaline solution; the former immediately assumes a green tint: and by attending to the change effected by the addition of the acid, and noticing the point when blueness is again restored to the cabbage-colour, or when the litmus becomes reddened, the indication of neutrality is sufficiently evident and accurate for general purposes. The test by papers is, however, more precise.

A process of neutralization, quite the same in principle, may be adopted for the purpose of estimating the strength of *acids*, but from circumstances it is not often used, and being easily comprehended from the above directions, claims no further notice here.

The common mode of purifying pearlash consists in pouring upon it its weight of cold water, and stirring the mixture occasionally during twenty-four hours; the solution is then poured clear off the residuary salt, and evaporated to dryness. In this way much impurity is separated, the foreign salts being, with few exceptions, much less soluble than the alkaline; yet some of them are taken up, and the silicated potassa which rough pearlash always contains, is also dissolved. The carbonate from tartar is more pure, but often contains lime. The purest carbonate is undoubtedly that obtained by exposing the crystallized bicarbonate to heat sufficient to expel its water and half of its carbonic acid; the salt is then dissolved in water, which generally leaves some silica, that has been rendered insoluble by the exposure to heat. If the salt be fused, this silica combines with the potassa and expels a portion of carbonic acid, so

that although a certain degree of heat is required to drive off the excess of carbonic acid, and render the silica insoluble, too much heat causes it again to be taken up, and rendered soluble in water. With these precautions, upon evaporating the solution to dryness in a silver basin, a very pure carbonate of potassa is obtained. Carbonate of potassa is also formed, as already stated, when two parts of powdered tartar (bitartrate of potassa) and one of nitrate of potassa, thoroughly mixed, are deflagrated in successive portions in an iron ladle or crucible. The residue (often called *black flux*) is lixiviated and evaporated as usual. Equal parts of nitre and tartar, treated in the same way, furnish *white flux*, in which the whole of the charcoal is destroyed by combustion. These fluxes are of much use in certain metallurgical operations, contributing to the fusibility of refractory earthy compounds*.

BICARBONATE OF POTASSA ($P + 2\text{car}'$) is formed by passing a current of carbonic acid into a solution of the pure carbonate. By evaporation at a very moderate heat, crystals are obtained in the form of four-sided prisms, with dièdral summits. They are not deliquescent. Their primary form, which according to Brooke is a right oblique-angled prism, and their cleavages, have been described by Levy in the *Quarterly Journal*, xv. 286, and by Brooke (*Ann. of Phil.*, N.S., vi. 42). Their taste is only slightly alkaline, and they require for solution four parts of water, at 60° . Boiling water dissolves nearly its own weight of the crystals, but during the solution a portion of carbonic acid is evolved. Exposed to a red-heat, they evolve carbonic acid and water, and carbonate of potassa remains. This salt was first observed by Dr. Wollaston to contain exactly twice the quantity of carbonic acid existing in the carbonate. (*Phil. Trans.*, 1808.)

It contains, according to Berard, 9 per cent. of water. Crystallized bicarbonate of potassa, therefore, consists of

	Berard.			
Potassa	1	48	47.53	48.92
Carbonic acid	2	44	43.56	42.01
Water	1	9	8.91	9.07
<hr/>				
Crystals of bicarbonate of potassa	1	101	100.00	100.00

Graham represents this salt as a double carbonate of potassa and water by the formula $(h + o) + (car + 2o) + (po + o) + (car + 2o)$. Its analysis by Kirwan and Pelletier would indicate *two* atoms of water.

It is generally stated that during the saturation of silicated carbonate of potassa with carbonic acid, the whole of the silica is precipitated; but this is not the case; and it will be found that during the crystallization

* The purified Carbonate of Potassa of the shops should be perfectly soluble in twice its weight of cold water. It often contains silica, sulphate of potassa, chloride of potassium, and carbonate of lime. To detect these, dissolve a hundred grains in excess of nitric acid diluted with eight parts of water; the silica, if any be present, remains undissolved, or may be rendered insoluble by evaporation: separate the solution into three equal parts; to

the first, add nitrate of baryta, which causes a precipitate of sulphate; collect, wash, and dry it; 100 parts are equivalent to 74 of sulphate of potassa: to the second, add nitrate of silver; 100 grains of the precipitate, washed and dried at a dull red-heat, are equivalent to 52 of chloride of potassium: to the third, add oxalate of ammonia, and dry the edulcorated precipitate at a heat of 300° ; 100 parts are equal to 77 of carbonate of lime.

of the salt, an additional deposition of silica ensues. When the crystals of bicarbonate have been redissolved, and a second or third time crystallized, the silica is excluded.

The following proportions may be used for the preparation of bicarbonate of potassa upon the large scale: 100 lbs. of purified carbonate of potassa are dissolved in 17 gallons of water, which, when saturated with carbonic acid, yield from 35 to 40 lbs. of crystallized bicarbonate; 50 lbs. of carbonate of potassa are then added to the mother-liquor, with a sufficient quantity of water to make up 17 gallons, and the operation repeated. (HENNELL.)

The carbonate and bicarbonate of potassa are both decomposed by quick-lime, which deprives them of carbonic acid; hence the use of that substance in the process for obtaining pure *potassa*. They are also decomposed by the greater number of acids, which unite with the alkali, the carbonic acid being expelled with effervescence.

SESQUICARBONATE OF POTASSA.—When the solution of the bicarbonate is boiled until carbonic acid no longer escapes, it loses one-fourth of its acid, and on cooling forms deliquescent crystals, insoluble in alcohol. The same salt is obtained by dissolving 100 parts of carbonate and 131 of bicarbonate of potassa in water. This salt was first mentioned by Berthollet in 1809. (BERZELIUS.) It is probably identical with that noticed by Thomson (*Princip. of Chem.*, ii. 225), who states it to consist of

Potassa	1	48	35.56
Carbonic acid	$1\frac{1}{2}$	33	24.44
Water	6	54	40.00
<hr/>					
Crystallized sesquicarbonate of potassa	1		135		100.00

POTASSIUM AND CYANOGEN. CYANURET OF POTASSIUM. CYANIDE OF POTASSIUM. (*po + cy*) or K Cy.—This compound is obtained by passing a current of cyanogen over heated potassium; the metal absorbs the gas with ignition, and yields a yellowish-gray cyanuret. It is also formed by saturating a concentrated solution of caustic potassa with hydrocyanic acid, and boiling down in a retort till crystallization commences; the liquid is then poured into a porcelain capsule and heated till the residue is of a dull-red heat. Another mode of obtaining cyanuret of potassium, and perhaps the best, consists in reducing the crystallized ferrocyanuret of potassium to powder, drying it, and heating it to redness in a covered iron vessel, letting it cool excluded from air, bruising the porous fused mass, putting it into a glass funnel, moistening it with spirit of wine, and then lixiviating it with cold water; the first runnings are colourless and concentrated, and should be rapidly evaporated to dryness and fused in a porcelain capsule: or the fused mass may be boiled in weak alcohol, and on cooling pure cyanuret of potassium is deposited. A spirit of wine containing 60 per cent. of alcohol, largely dissolves cyanuret of potassium at its boiling-point, but lets nearly the whole fall as it cools: stronger or weaker alcohol retains much more in permanent solution. According to Wigger, cyanuret of potassium is also obtained by the transmission of hydrocyanic vapour from a mixture of ferrocyanuret of potassium and sulphuric acid, into a concentrated alcoholic solution of potassa; as soon as it is saturated, the cyanuret precipitates in the form of a crystalline powder. (LIEBIG.)

When animal substances, such as horn or dried blood, are calcined at a red-heat, with half their weight of carbonate of potassa, so long as a blue flickering flame burns upon the surface, and after the mass has cooled, if it be lixiviated with a small quantity of water, a solution of carbonate with cyanuret of potassium is obtained, which, when filtered, precipitated with acetate of lime, again filtered, and mixed with alcohol, yields a precipitate of cyanuret of potassium.

Cyanuret of potassium should be carefully preserved out of the contact of air and water; it may be fused without decomposition, provided air be excluded, and is not changed by a red-heat; but with the access of oxygen it becomes cyanate of potassa; after fusion it often crystallizes in cubes; its taste is pungent and alkaline, accompanied with the flavour of hydrocyanic acid. It is very soluble in water, and very little soluble in absolute alcohol, so that the latter throws it down from its recent and cold aqueous solution; exposed to air it becomes moist and smells of hydrocyanic acid: it is very poisonous. Its solution is decomposed by the acids and by heat: the former resolve it into potassa and hydrocyanic acid: when heated, its elements enter into new combinations, producing ammonia, and carbonic and hydrocyanic acids.

When cyanuret of potassium effervesces with the acids, it contains carbonate of potassa: a yellow tint indicates the presence of iron; if it blackens when calcined, it is contaminated by formiate of potassa. (LIEBIG.) It consists of

Carbon	2	.	12	.	18.25	} Cyanogen	1	.	26	.	39.50	.	40.24	Liebig.
Nitrogen	1	.	14	.	21.25									
Potassium	1	.	40	.	60.50		Potassium	1	.	40	.	60.50	.	59.76
<hr/>														
Cyanuret of potassium	1		66		100.00				1		66		100.00	100.00

CYANATE OF POTASSA ($po + o$) + ($2car + n + o$) or ($P + cy'$) is obtained by carefully heating a mixture of 4 parts of powdered dry ferrocyanuret of potassium, and 1 of peroxide of manganese to dull redness: when cold, the fused mass is powdered, and boiled in alcohol of 0.86, which dissolves the cyanate and deposits it on cooling. Cyanate of potassa is also formed by simply heating finely pulverized ferrocyanuret of potassium to redness in an open iron pan, and continually stirring so as to expose it to the air; it absorbs oxygen, and when it begins to agglutinate in consequence of the fusion of the cyanate, it is powdered and digested in hot spirit of wine of sp. gr. 0.86. On cooling the filtered solution it deposits crystals of cyanate of potassa. Another source of this salt, discovered by Liebig, consists in adding melam, ammeline, or ammelide, to hydrate of potassa fused in a silver basin. (See pp. 576 and 578.)

This salt is decomposed both by water and acids, which convert the cyanic acid into carbonic acid and ammonia; in fact, by exposure to air it exhales ammonia, and, without changing form, becomes bicarbonate of potassa. It crystallizes in small plates like chlorate of potassa; tastes like saltpetre; is anhydrous; and in close vessels excluded from air and moisture, may be fused without decomposition. (WÖHLER, *Ann. de Ch. et Ph.*, xx 353, and xxvii. 196.) When fused with potassium it yields a mixture of cyanuret of potassium and potassa; and with sulphur, a mixture of sulphocyanuret of potassium, sulphuret of potassium, and

sulphate of potassa. When triturated with oxalic acid, both being dry, oxalate of potassa is formed, and the evolved cyanic acid passes into that form of cyanuric acid which has been called *cyamelide* (p. 566). Cyanate of potassa consists of

Potassa	1	48	53.5	53.95
Cyanic acid	1	34	41.5	40.05
Cyanate of potassa	1	82	100.0	100.00

Wöhler.

SULPHOCYANURET OF POTASSIUM. ($po + n + 2 car + 2 s$).—When 5 parts of dry ferrocyanuret of potassium, 5 of sulphur, and 1 of carbonate of potassa, are well mixed in fine powder and exposed to nearly a red-heat, the mixture fuses and takes fire; it should be stirred as long as it continues to burn, and kept for a few minutes in fusion. The residue, digested in hot water and filtered, furnishes a solution, which, evaporated to dryness, affords *sulphocyanuret of potassium*; sulphuret of iron remains upon the filter. The sulphocyanuret may be purified by digestion in alcohol, which dissolves it and leaves any carbonate of potassa that might have been mixed with it. The alcoholic solution when evaporated, leaves the pure salt, which, redissolved in water and concentrated by evaporation, yields prismatic crystals which are of a cooling saline taste, deliquescent, and anhydrous, being in form, taste, and fusibility, very analogous to nitre: they are soluble in boiling alcohol.

Whether, when dissolved in water, this salt is to be considered as sulphocyanate of potassa, is a question similar to that which applies to the analogous conversion of the sulphurets into hydrosulphates. Distilled with phosphoric acid, the sulphocyanic acid passes over, and phosphate of potassa remains in the retort. Its aqueous solution is a delicate test of the presence of peroxide of iron, which it throws down of a blood-red colour; and the solution of the sulphocyanuret often acquires a pinkish tinge from the presence of a trace of iron.

Sulphocyanuret of potassium is a compound of

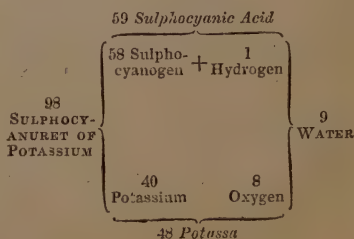
Potassium	1	40	40.8	40.33
Sulphocyanogen	1	58	59.2	59.67
Sulphocyanuret of potassium	1	98	100.0	100.00

Berzelius.

Its ultimate constituents, therefore, are

Potassium	1	40	40.8
Sulphur	2	32	32.7
Nitrogen	1	14	14.3
Carbon	2	12	12.2
Sulphocyanuret of potassium	1	98	100.0

And assuming that, by the action of water, the potassium forms potassa, and sulphocyanogen sulphocyanic (or rather hydrosulphocyanic) acid, then the annexed diagram will represent the change.



SELENIOCYANURET OF POTASSIUM. ($po + n + {}^2car + {}^2se.$)—Berzelius formed this salt by heating a mixture of ferrocyanuret of potassium and selenium, and washing the fused mixture: by evaporation, anhydrous crystals of the *seleniocyanuret* were obtained.

POTASSIUM AND BORON.—When boracic acid is reduced by fusion with potassium, a brown mass results, which evolves hydrogen in water; probably, however, only from adhering potassium.

BORATE OF POTASSA ($P + bo'$) is a salt which has been scarcely examined: it may be prepared by boiling boracic acid in solution of potassa, or by exposing a mixture of boracic acid and nitre to a bright red-heat; it furnishes by solution and evaporation quadrangular prisms, permanent in the air. It combines with excess of base to form a *diborate*.

BOROFLUORIDE OF POTASSIUM is obtained, according to Berzelius, by adding fluoboric acid to a solution of fluoride of potassium: a gelatinous precipitate falls, which, collected upon a filter, becomes opaque, and feels, whilst moist, like powdered starch. When dry, it has a bitterish taste; it does not redden litmus. 100 parts of cold water only dissolve 1.4 of this salt; but it is more soluble in boiling water, and, as the solution cools, it deposits it in small anhydrous crystals. It requires a high heat, long continued, for its decomposition, and is ultimately resolved into fluoboric gas and fluoride of potassium.

THE SALTS OF POTASSIUM are upon the whole readily soluble in water, though less so than the salts of ammonia. They afford no precipitates with pure or carbonated alkalis. They produce a precipitate in solution of chloride of platinum. They are not changed by sulphuretted hydrogen, nor by ferrocyanuret of potassium. Added to sulphate of alumina, they enable it to crystallize, so as to form alum. The solution of potassa (and of most of its salts) is well characterized by the action of tartaric acid and of fluosilicic acid: a strong solution of tartaric acid added to a strong solution of potassa or of a salt of potassa causes no precipitate till the point of neutralization is exceeded; excess of the acid then produces a crystalline precipitate of *bitartrate of potassa*: when the solutions are dilute the precipitate is slowly formed and the crystals more apparent: the precipitate is dissolved by the addition of hydrochloric, nitric, sulphuric, or oxalic acid, but not by tartaric, or by acetic acid. Solutions of carbonated and caustic potassa, soda, and ammonia, dissolve the precipitate with ease, but the addition of a small quantity of a strong acid reproduces it, and it is again dissolved by a greater quantity of the same acid. Fluosilicic acid produces a transparent gelatinous precipitate in solutions of potassa and of its salts, which is iridescent when it subsides, and dries into a white powder. Free hydrochloric acid renders it opalescent. An alcoholic solution of carbazotic acid produces a yellow crystalline precipitate in solutions of potassa and its salts. The neutral soluble salts of potassa may for the most part be heated to redness without suffering decomposition, especially if air be excluded. In using the test of chloride of platinum to detect potassa salts, the absence of ammoniacal salts must be previously ascertained, as they generally produce analo-

gous effects upon that re-agent: or the platinum test may be applied after the salt has been subjected to a red heat, by which the salts of ammonia will have been decomposed or evaporated.

§ II. SODIUM.

SODIUM, (Natrium of the German chemists,) discovered by Sir H. Davy in 1808, was obtained from soda, by an operation analogous to that for procuring potassium from potassa, by the gun-barrel; but the hydrate of soda is more difficult of decomposition than that of potassa, and the product of metal less certain and abundant: it may be facilitated, according to Thenard, by fusing the soda with a small proportion of potassa; so that an alloy of sodium and potassium distils over, which may be decomposed by keeping it in an open vessel, covered with oil or turpentine or with a film of naphtha; the potassium becomes oxidized, and the sodium remains pure and metallic. Sodium may also be obtained by heating an intimate mixture of charcoal and carbonate of soda in an iron bottle, as in the corresponding process for potassium; this mixture is usually prepared by calcining acetate of soda.

SODIUM is soft, malleable, and easily sectile; it does not, like potassium, become brittle at 32° , but even at that low temperature several globules may be welded together by pressure. Its specific gravity, according to Davy, is 0.9348; according to Gay Lussac and Thenard, it is 0.972 at 59° . In colour it resembles silver, but instantly tarnishes on exposure to air. It softens at about 122° : it fuses at about 190° , and is volatile at a white heat. It burns with a yellow flame when heated in contact with air, and requires the same cautions to preserve it from spontaneous oxidizement as potassium.

SODIUM AND OXYGEN. PROTOXIDE OF SODIUM. SODA. ($SO + O$) or S, or Na O, or Na.—The affinity of sodium for oxygen appears to be somewhat less than that of potassium. When sodium is thrown upon water, it produces violent action, but the metal does not in general inflame, unless the quantity of water be very small, so as to diminish its cooling power; it inflames for instance if a thin slice of it be placed upon a piece of moistened paper; in this case, hydrogen is evolved and soda is formed. By the quantity of hydrogen evolved, during this action of sodium on water, we learn that soda consists of about 74.6 sodium, and 25.4 oxygen *per cent.*; and, if it be considered as the protoxide, the number representing the metal will be 24 (23.3 GMELIN and TURNER), and anhydrous soda will consist of

					Davy.
Sodium . . .	1 . .	24 . .	75 . .	74.6	
Oxygen . . .	1 . .	8 . .	25 . .	25.4	
Soda	1	32	100	100.0	

Anhydrous soda is obtained in the same way as anhydrous potassa, and resembles it in appearance, but is less fusible and less volatile.

PEROXIDE OF SODIUM. SESQUIOXIDE OF SODIUM. ($SO + 1\frac{1}{2}O$).—By heating sodium in oxygen, it burns vividly, and a yellowish-green *peroxide* is formed, which, by the action of water, evolves oxygen, (as is the case with peroxide of potassium,) and produces a solution of the protoxide.

Peroxide of sodium is composed, according to Davy, of an atom of sodium and an atom and a half of oxygen, or $(2SO + 3O)$, but according to Millon it consists of 1 of sodium and 2 of oxygen $(SO + 2O)$.

HYDRATE OF SODA OR CAUSTIC SODA $(SO + O) + (h + O)$ or $(S + q)$, as it usually occurs in the laboratories, is obtained from the *carbonate*, by the action of lime and alcohol, as described under the head *Potassa*. Its colour is grayish-white; its specific gravity is 2.0 (DALTON); it requires a red heat for fusion; and when intensely heated upon charcoal, as by the oxygen or oxyhydrogen blowpipe, it evaporates and tinges the flame yellow. It has the same general characters as hydrate of potassa: like it, it retains water at a red heat, and is deprived of it by the same means. It consists of

					Davy.
Soda	. . .	1	. . .	32	. . . 78.1 . . . 77.1
Water	. . .	1	. . .	9	. . . 21.9 . . . 22.9
Hydrate of soda 1				41	100.0 100.0

Like potassa, it may be obtained in crystals from its concentrated aqueous solution, containing a larger relative quantity of water.

The following Table by Dalton shows the proportion of anhydrous soda in solutions of different specific gravities:—

Specific gravity of solution.	Dry Soda per cent. by weight.	Boiling point.	Specific gravity of solution.	Dry Soda per cent. by weight.	Boiling point.
1.85	63.6	600°	1.36	26.0	235°
1.72	53.8	400	1.32	23.0	228
1.63	46.6	300	1.29	19.0	224
1.56	41.2	280	1.23	16.0	230
1.50	36.8	265	1.18	13.0	217
1.47	34.0	255	1.12	9.0	214
1.44	31.0	248	1.06	4.7	213
1.40	29.0	242			

Hydrated soda is distinguished from hydrated potassa, by forming an *efflorescent* paste when exposed to the atmosphere: potassa, under the same circumstances, *deliquesces*. If excess of tartaric acid be added to a solution of soda there is no precipitation; but in solution of potassa it occasions a deposit of a number of minute crystals. Solution of soda occasions no precipitate when added to solution of chloride of platinum. Solution of potassa occasions a yellow precipitate in solution of platinum. In combination with acids it produces a perfectly distinct class of salts; its affinity for the acids is a little inferior to that of potassa.

CHLORIDE OF SODIUM. SEA SALT. MURIATE OF SODA. $(SO + C)$ or $Na Cl$.—Sodium when heated in chlorine burns vividly, and produces this compound. It consists of

				Ure.
Sodium	. . .	1	. . . 24	. . . 40 . . . 39.98
Chlorine	. . .	1	. . . 36	. . . 60 . . . 60.02
Chloride of sodium 1			60	100 100.00

Chloride of sodium is decomposed when heated with potassium: sodium and chloride of potassium are the results. (DAVY.)

When hydrate of soda is heated in chlorine, oxygen and water are evolved, and chloride of sodium formed; when heated in hydrochloric acid gas, the water of the hydrate is first expelled, and then the oxygen of the

soda combines with the hydrogen of the hydrochloric acid to form water, and the sodium and chlorine unite to form the chloride.

Common salt exists abundantly in nature both as a solid fossil (*sal gemme*), and dissolved in spring water, and in the ocean. Extensive beds of it are found in Cheshire, where it is known under the name of *rock-salt*. From these sources the immense demands are supplied; that is, either by evaporating brine-springs, or sea-water, or quarrying it from the mine.

When heated, chloride of sodium falls into pieces with a crackling noise, or *decrepitates*. At a red-heat it fuses without undergoing any decomposition, and on cooling concretes into a hard white mass; at a bright-red heat it sublimes in the air, and tinges flame of a blue colour. It is nearly or quite insoluble in absolute alcohol. In the solubility of common salt in water there is this peculiarity, that it is taken up nearly in the same proportion by cold and by hot water; so that, although its solution deposits crystals during evaporation, it does not do so by cooling. According to Berzelius, 1 part of salt dissolves in $2\frac{1}{4}$ of water at 60° , and in $2\frac{1}{3}$ of water at 212° . According to Gay Lussac, 100 parts of water at 58° dissolve 36 of salt; at 140° , 37 parts; and at 225° , which is the boiling-point of a saturated solution, 100 parts of water dissolve 40.38. At 32° water dissolves rather more than at 60° .

When pure, chloride of sodium does not alter by exposure to air, though it is generally more or less deliquescent, from containing chlorides of magnesium and of calcium: obtained by slow or spontaneous evaporation, it crystallizes in solid cubes; but when procured, as is usually the case, at a boiling heat, by removing its crystals from the surface of its solution whilst evaporating, it exhibits the form of a hollow quadrilateral pyramid. The crystals are anhydrous, though they often include a little interstitial water. Its specific gravity is 2.125. A concise account of the different methods of manufacturing salt will be found in AIKIN'S *Dictionary*, Art. MURIATE OF SODA. See also DUMAS, *Chim. App. aux Arts*, ii. 449, and URE, *Dict. of Arts and Manuf.* Dr. Henry states (*Phil. Trans.*, 1810) that the various forms under which salt is known in commerce, such as *bay-salt*, *fishery-salt*, &c., arise from modifications in the size and hardness of the grain, and not from any essential difference of composition. The following table includes his general results:—

1000 Parts by Weight consist of									
Kind of Salt.	Insoluble Matter.	Muriate of Lime.	Muriate of Magnesia.	Total Earthy Muriates.	Sulph. of Lime.	Sulph. of Magnesia.	Total Sulphates.	Total Impurity.	Pure Muriate of Soda.
Cheshire Brit. Salt fr. For. Bay Salt. Sea-water.	St. Ube's	9	trace	3	3	23 $\frac{1}{2}$	4 $\frac{1}{2}$	28	960
	St. Martin's	12	do.	3 $\frac{1}{2}$	3 $\frac{1}{2}$	19	6	40 $\frac{1}{2}$	959 $\frac{1}{2}$
	Oleron	10	do.	2	2	19 $\frac{1}{2}$	4 $\frac{1}{2}$	23 $\frac{3}{4}$	964 $\frac{1}{4}$
	Scotch (common) . .	4	—	28	28	15	17 $\frac{1}{2}$	32 $\frac{1}{2}$	935 $\frac{1}{2}$
	Scotch (Sunday) . .	1	—	11 $\frac{1}{2}$	11 $\frac{1}{2}$	12	4 $\frac{1}{2}$	16 $\frac{1}{2}$	971
	Lymington (com.) . .	2	—	11	11	15	35	50	937
	Ditto (cat)	1	—	5	5	1	5	6	988
	Crushed rock	10	0 $\frac{1}{10}$	0 $\frac{3}{10}$	0 $\frac{4}{10}$	6 $\frac{1}{2}$	—	6 $\frac{1}{2}$	983 $\frac{1}{4}$
	Fishery	1	0 $\frac{1}{4}$	0 $\frac{3}{4}$	1	11 $\frac{1}{4}$	—	11 $\frac{1}{4}$	986
	Common	1	0 $\frac{1}{4}$	0 $\frac{3}{4}$	1	14 $\frac{1}{2}$	—	14 $\frac{1}{2}$	983 $\frac{1}{2}$
	Stoved	1	0 $\frac{1}{4}$	0 $\frac{3}{4}$	1	15 $\frac{1}{2}$	—	15 $\frac{1}{2}$	982 $\frac{1}{2}$

Chloride of sodium is decomposed by moist carbonate of ammonia; bicarbonate of soda, sal-ammoniac, and free ammonia are formed; with moist carbonate of potassa, it yields chloride of potassium and carbonate of soda (which see). In the process for obtaining hydrochloric acid it is decomposed by sulphuric acid. In this decomposition, the oxygen of the water of the sulphuric acid is transferred to the sodium of the salt, the chlorine of which combines with the hydrogen of the water to produce hydrochloric acid gas. The oxide of sodium unites with the dry sulphuric acid to produce sulphate of soda (see the diagram under *Sulphate of Soda*). Chloride of sodium is also decomposed by nitric acid; effervescence ensues, chlorine tinged with nitrous acid is evolved, and provided a sufficiency of nitric acid has been used, pure nitrate of soda remains on evaporation to dryness. When chloride of sodium is triturated with crystallized oxalic acid and heated, it is also decomposed; hydrochloric acid is evolved, and oxalate of soda formed, so that when the residue is heated to redness, carbonate of soda remains. When chloride of sodium and ferruginous clay are heated together, the silica and alumina of the clay are vitrified by the soda of the salt, and its chlorine combines with the iron; it is upon this principle that it is used as a glaze for stoneware, being thrown into the furnaces or ovens in which the articles are baked, it is volatilized, and decomposed upon their surfaces.

Common salt is of most extensive use as a preservative of food, and as a condiment, as a source of soda and of hydrochloric acid and chlorine, and for various agricultural and horticultural purposes. (*Quarterly Journal*, x. 52.) Glauber first obtained hydrochloric acid from it, and the existence of soda in it was first shown by Duhamel. Davy first demonstrated its true constitution.

CHLORIDE OF SODA. CHLORITE OF SODA. HYPOCHLORITE OF SODA.—These names have been applied to a compound formed by passing chlorine into a cold and dilute solution of caustic soda, or by decomposing chloride of lime by carbonate of soda (as suggested by PAYEN, *Quart. Jour.*, N.S., i. 236). It is powerfully bleaching and smells of chlorine: exposed to air it absorbs carbonic acid and evolves chlorine, hence it may be used as a disinfectant. When heated, it undergoes changes similar to those produced by passing chlorine into a strong solution of soda, that is, chlorate of soda and chloride of sodium are formed. A formula in which chlorine is passed into a solution of *carbonate of soda* is given in the Pharmacopœia (*Liquor sodæ chlorinatæ*); it is more stable than the corresponding potassa compound, and therefore preferred for medical use as a disinfectant. It contains chlorite of soda, chloride of sodium, bicarbonate of soda, and carbonate of soda. (DUMAS.)

CHLORATE OF SODA ($S + Cl$) was procured by Chenevix, (*Phil. Trans.*, 1802,) by the same process as chlorate of potassa, but not possessing less solubility than chloride of sodium the two substances are difficultly separable. Vauquelin obtained it by saturating chloric acid with soda. It is also formed by mixing strong solutions of bitartrate of soda and chlorate of potassa, when bitartrate of potassa precipitates, and chlorate of soda remains in solution. Its crystals resemble those of chlorate of potassa; its taste is also nearly similar. It dissolves in three

parts of cold water, and in somewhat less at 212° . It is more soluble in hydrated alcohol than chloride of sodium; hence that solvent is sometimes used to separate the two compounds. It is slightly deliquescent in very damp weather. The crystals are anhydrous, and consist of

Soda	1	32	29.65
Chloric acid	1	76	70.35
<hr/>			
Chlorate of soda	1	108	100.00

IODIDE OF SODIUM. ($so + i$).—Iodine and sodium act upon each other with the same phenomena as in the case of potassium. Iodide of sodium may also be formed by adding iodine to a solution of caustic soda and evaporating to dryness, and fusing the residue. It is contained in the mother-liquor of kelp, in the ashes of burned sponge, &c., and in those cases is resorted to as a source of iodine, and is decomposed by sulphuric acid and oxide of manganese (p. 371). When hydriodic acid is saturated with soda or carbonate of soda, we obtain a deliquescent salt which crystallizes in flat rhomboidal prisms; when heated, it fuses and loses water of crystallization. The residue is iodide of sodium. When intensely heated it becomes slightly alkaline, and is volatilized. 100 parts of water at 60° dissolve 173 of this iodide. It is also soluble in alcohol. It consists, when anhydrous, of

Sodium	1	24	16
Iodine	1	126	84
<hr/>			
Iodide of sodium	1	150	100

IODATE OF SODA ($so + o$) + ($i + 5o$) or ($S + i'$) is made by dissolving iodine in solution of soda; a white compound forms, which is the iodate with a portion of iodide of sodium; the latter may be removed by alcohol, which does not dissolve the iodate. 100 parts of water at 60° dissolve 7.3 of this salt. It forms small prismatic tufted crystals, which, when heated, afford oxygen and iodide of sodium. (GAY LUSSAC, *Ann. de Ch.*, xci.) When iodine is dissolved in a weak solution of soda till the liquor begins to redden, and left to spontaneous evaporation, hexangular prismatic crystals of *iodite of soda* are formed, soluble without decomposition in cold water, but resolved by hot water and by alcohol into iodate of soda and iodide of sodium. (DUMAS.)

BROMIDE OF SODIUM. ($so + b$).—Sodium and bromine act upon each other with much intensity; the result is a fusible compound, soluble in water and in alcohol, and crystallizing at 86° in anhydrous cubes, but at lower temperatures in hexagonal tables, containing 26.37 per cen. of water. The *anhydrous bromide* consists of

Sodium	1	24	23.53
Bromine	1	78	76.47
<hr/>			
Bromide of sodium	1	102	100.00

And the hexagonal *hydrate* of

Anhydrous bromide . . .	1	102	73.91	Mitscherlich.
Water	4	36	26.09	26.37
<hr/>				
	1	138	100.00	100.00

When bromine acts upon solution of soda, bromide of sodium and *bromate of soda* ($S + b/$) are the results.

FLUORIDE OF SODIUM ($SO + f$) is obtained by saturating hydrofluoric acid with soda, and evaporating to dryness; a white and difficultly-fusible compound results, the aqueous solution of which, when pure, furnishes cubical crystals, and acts upon glass. 100 parts of water dissolve 4 of this fluoride, and it is not more soluble in hot than in cold water. It may also be obtained by mixing 10 parts of silico-fluoride of sodium with 11.2 of dry carbonate of soda and sufficient water to form a thin paste, which, when boiled, evolves carbonic acid, and concretes. When cold, it must be powdered and boiled with more water as long as it effervesces; then filtered and evaporated (in silver, as it acts on glass,) till it crystallizes; the crystals must be redissolved and again formed, in order to separate adhering silica. During the formation of the crystals by slow evaporation, they exhibit the same luminous appearance as sulphate of potassa. When they retain any carbonate of soda, they are octoëdral, but when pure, always cubic. They are insoluble in alcohol. Berzelius obtained a crystallizable compound of this salt with hydrofluoric acid. Fluoride of sodium consists of

Sodium	. . .	1	. . .	24	. . .	57.1
Fluorine	. . .	1	. . .	18	. . .	42.9
<hr/>						
Fluoride of sodium		1		42		100.0

NITRATE OF SODA. ($SO + O$) + ($n + 5 O$) or ($S + n/$). The *cubic nitre* of old writers. This salt, which may be obtained by neutralizing carbonate of soda by dilute nitric acid, crystallizes in rhomboids (BROOKE, *Ann. Phil.*, 2nd series, v. 452), soluble in 3 parts of water at 60° , in its own weight at 123° , and in less than its weight at 212° . (DUMAS.) Berzelius says that one part dissolves in two of water at 60° , and Gay Lussac (*Cours de Chimie*, Paris, 1828) asserts that 100 parts of water at 32° dissolve 73 parts; and at 212° , 173 parts. Its solubility, as given upon the authority of Marx (THOMSON'S *System*, ii. 448), is as follows: 100 of water at 32° dissolve 80, at 50° 22.7, at 61° 55, and at 246° 218.5. So that, according to this account, its solubility at 32° is more than three times greater than at 50° . It has a cool sharp flavour, and is somewhat deliquescent in damp air, and therefore unfit for the manufacture of gunpowder. Berzelius found a mixture of 5 nitrate of soda, 1 charcoal, and 1 sulphur, to burn three times more slowly than a similar mixture with nitrate of potassa: its flame is orange-coloured. It is often found in crude nitre, resulting partly, perhaps, from the decomposition of common salt. Large quantities of *native nitrate of soda* have been discovered in Peru, forming a stratum covered with clay and alluvium of many miles in extent, and it now forms a considerable article of trade. It may be employed in fire-works, and used as a substitute for nitre (it being cheaper) in the manufacture of nitric acid, of sulphuric acid, and in other cases in which large quantities of nitre are consumed. It is too expensive as a source of soda. It is a good deal employed as a manure, but with doubtful advantage, so far at least as regards wheat. Nitrate of soda is anhydrous, and consists of

Soda . . . 1 . . . 32 . . . 37.2 . . . 37.5	Wenzel.
Nitric acid . . 1 . . . 54 . . . 62.8 . . . 62.5	
Nitrate of soda . 1 . . . 86 . . . 100.0 . . . 100.0	

SODIUM AND AMMONIA. SODIAMIDE.—When sodium is heated in ammoniacal gas, hydrogen is disengaged, and an olive-coloured fusible substance formed, composed apparently of sodium and amidogen ($SO + n + 2h$). (See *Potassiamide*, p. 627.)

SODIUM AND SULPHUR.—The account of the action of sulphur on potassium and potassa, and of sulphuretted hydrogen upon solution of potassa, applies generally to sodium and soda, and their corresponding compounds. Sodium and sulphur combine when gently heated, with vivid ignition, and form a *sulphuret of sodium* ($SO + S$). And the same compound may be obtained by the decomposition of sulphate of soda by hydrogen or by charcoal. Sulphuret of sodium is composed of

Sodium 1 . . . 24 . . . 60
Sulphur 1 . . . 16 . . . 40
1 . . . 40 . . . 100

BISULPHURET OF SODIUM ($SO + 2S$) is similarly constituted to the corresponding compound of potassium.

A concentrated aqueous solution of sulphuret of sodium yields square prismatic crystals of *hydrosulphuret of soda*, which, when heated, fuse in their water of crystallization and leave a white anhydrous salt. The solution, exposed to air, rapidly absorbs oxygen, and becomes a hyposulphite. The hydrosulphurets of soda derive some additional interest as being produced, upon the large scale, in the principal processes for obtaining soda by the decomposition of the sulphate of soda, as will presently be stated.

HYPOSULPHITE OF SODA ($S + S$) is formed by exposing a solution of persulphuret of sodium to the atmosphere till it becomes colourless; or by adding a solution of carbonate of soda to hyposulphite of lime, and filtering. It crystallizes in silky tufts, and when the solution is concentrated the whole concretes into a crystalline mass. It deliquesces in the air, but under a vacuum with sulphuric acid it effloresces. Its taste is bitter and nauseous; when heated it fuses, dries, and takes fire, deflagrating with a yellow flame. It is insoluble in alcohol, which precipitates it from its aqueous solution. It readily dissolves chloride of silver. (HERSCHEL, *Edinb. Phil. Jour.*, i. 19.)

SULPHITE OF SODA ($S + S$) is crystallizable in transparent four and six-sided prisms, soluble in four parts of water at 60° , and in less than its weight of boiling-water. It consists of 32 soda + 32 sulphurous acid = 64. The crystals contain 8 atoms of water = 72. There is also a crystallizable *bisulphite of soda*, obtained by passing a current of sulphurous acid gas through a solution of carbonate of soda till the liquid reddens vegetable blues: it yields on evaporation four-sided rectangular prisms, having a sulphurous taste and smell, and reddening vegetable blues. (THOMSON, ii. 447.) Its formula according to Clark is $2(S + 2O) + (SO + O) + 9q$.

HYPOSULPHATE OF SODA ($S+S'$) may be obtained by decomposing hyposulphate of baryta by sulphate of soda; or hyposulphate of manganese may be decomposed by sulphuret of sodium, and the liquid evaporated to the point of crystallization: it forms transparent four-sided prisms of a peculiar bitterish taste, soluble in 2.1 of water at 60° , and in 1.1 at 212° , and insoluble in alcohol. According to Heeren (POGGEND. *Annalen*, vii. 77), they contain

Soda	1	32	26.23
Hyposulphuric acid	1	72	59.02
Water	2	18	14.75
Crystallized hyposulphate of soda	1	122	100.00

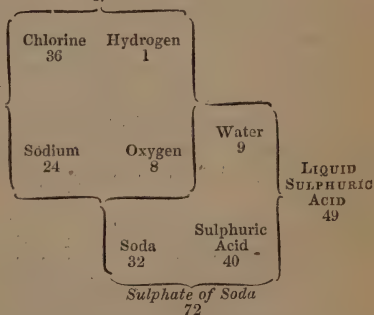
SULPHATE OF SODA ($S+S'$); GLAUBER'S SALT; SAL MIRABILE; is abundantly produced in various processes of the arts, by the action of sulphuric acid upon chloride of sodium, which consists of 24 sodium + 36 chlorine. Sulphuric acid consists of 40 dry acid + 9 water. The water of the acid, consisting of 1 hydrogen + 8 oxygen, is decomposed. Its hydrogen is transferred to the chlorine to produce hydrochloric acid (1 hydrogen + 36 chlorine), and its oxygen unites to the sodium, forming dry soda (8 oxygen + 24 sodium). The 40 dry sulphuric acid unite to the 32 soda, to produce sulphate of soda, which will be represented by the number 72.

Hydrochloric Acid

37

This decomposition is perhaps more clearly shown in the annexed diagram; the original substances being printed in capitals, the products in italics, and the components in common type: the numbers are the equivalent weights of 1 atom of the respective substances.

COMMON
SALT
60



Sulphate of soda is also a natural product. Casaseca found anhydrous sulphate of soda in the vicinity of Madrid; and Gimbernart discovered crystals of sulphate of soda in the Canton D'Argovie in Switzerland. It occurs in many mineral waters. It is also found in the ashes of some plants, and in some of the animal fluids. Sulphate of soda may be formed by saturating dilute sulphuric acid with carbonate of soda, and evaporating the solution. It crystallizes from its aqueous solution in large prisms, transparent, and efflorescent when exposed to air. The primary crystal is an oblique rhombic prism. (PHILLIPS, *Trans. Lond. Pharm.*) The specific gravity of the crystals is 1.349. (THOMSON.) Exposed to dry air, the crystals part with between 50 and 60 per cent. of water.

The *anhydrous* salt, as above stated, is composed of

Soda	1	32	44.4	Wenzel.
Sulphuric acid	1	40	55.6	55.7
Anhydrous sulphate of soda	1	72	100.0	100.0

And the ordinary crystals (decahydrated sulphate of soda) consist of

				Wenzel.	
Dry sulphate of soda	1	72	44.4	44.8	
Water	10	90	55.6	55.2	
<hr/>				<hr/>	
Crystallized sulphate of soda	1	162	100.0	100.0	

The taste of sulphate of soda is saline and somewhat bitter; it is soluble in rather less than three times its weight of water at 60° , and insoluble in alcohol. The solubility of sulphate of soda in water follows a singular law, first observed by Gay Lussac. (*Ann. de Ch. et Ph.*, xi.) After having increased rapidly to about the temperature of 92° , where it is at its maximum, it diminishes to 215° , and at that temperature the salt is nearly of the same solubility as at 87° .

At 32° 100 parts of water dissolve about 5 of anhydrous and 12 of crystallized salt.

50	10	26
60	11	31
70	16	48
77	28	99
87	43	215
92	50	322
104	48	291
122	46	262

When sulphate of soda is dissolved in its weight of boiling water, and a flask filled with it and tightly corked up, no crystallization generally ensues: but upon opening the flask it either immediately crystallizes, or does so upon touching the solution with a solid body. This experiment has already been referred to (p. 115). It sometimes, however, happens that a portion of the salt does crystallize, forming quadrangular crystals, which become opaque on exposure, and which, for sulphate of soda, are peculiarly hard; Mr. Faraday found these composed of

Dry sulphate of soda	1	72	50
Water	8	72	50
<hr/>			
Octohydrated sulphate of soda	1	144	100

If a solution of sulphate of soda, saturated at 91.5° , is evaporated at a higher temperature, opaque prisms of *anhydrous sulphate of soda* are deposited, the primary form of which is a rhombic octoëdron. Its specific gravity in this state is 2.462. (HAIDINGER.) 100 parts of water at the temperature of 57° dissolve 10.58 of this anhydrous salt, and when the solution is set aside, crystals of common Glauber's salt are formed. (THOMSON.)

When exposed to heat, sulphate of soda undergoes watery fusion; that is, it melts in its water of crystallization, and a portion of anhydrous salt is deposited: when the water has evaporated, the residue may be raised to a high heat, without undergoing decomposition. At a red-heat it fuses. The salt which has been deprived of its water by heat has an acrid taste, and produces a sense of heat upon the tongue in consequence of its absorbing water, which it does with great avidity.

Gay Lussac obtained a powerful pyrophorus, by igniting a mixture of lamp-black and dry sulphate of soda, analogous to that mentioned under

Sulphate of Potassa. (*Quarterly Journal*, iv. 208.) The decomposition of sulphate of soda for the manufacture of *carbonate of soda* is described under that salt.

BISULPHATE OF SODA ($S+2S'$) is obtained by adding sulphuric acid to a hot solution of sulphate of soda. It crystallizes in rhombic prisms, soluble in twice their weight of water at 60° , and containing water of crystallization. (LINK, CRELL'S *Annals*, 1796.) When a crystal of bisulphate of soda is held in the candle, it melts like ice. This salt liquifies at 300° , and may be kept at that temperature without much loss of weight. Its specific gravity is 1.8. At the temperature of 60° , one hundred parts of water dissolve 92.72 of this salt, so that it is twice as soluble as crystallized sulphate of soda. Its taste is very acid. (THOMSON, *Ann. Phil.*, x. 439, 2nd series.) An *anhydrous bisulphate of soda* may be obtained by gently heating together in a platinum crucible 10 parts of dry sulphate of soda, and 7 of sulphuric acid (specific gravity 1.85); the water of the acid escapes, and the residue may then be fused: it furnishes a very soluble but not a deliquescent salt, which, when distilled at a high temperature, affords *anhydrous sulphuric acid*. (BERZELIUS.) These salts consist of

Soda	1 . .	32 . .	28.57
Sulphuric acid	2 . .	80 . .	71.43
<hr/>			
Anhydrous bisulphate of soda	1	112	100.00

The crystallized bisulphate of soda contains

Soda	1 . .	32 . .	21.62
Sulphuric acid	2 . .	80 . .	54.05
Water	4 . .	36 . .	24.33
<hr/>			
Crystallized bisulphate of soda	1	148	100.00

SESQUISULPHATE OF SODA. ($S+1\frac{1}{2}S'$).—According to Thomson (*Ann. of Phil.*, 2nd series, x. 436), this salt is obtained when the residue after the decomposition of common salt by sulphuric acid in excess is dissolved in hot water and set aside; it usually forms the first crop of crystals; they are transparent prisms, firmer and harder than the common sulphate, of an acid taste, but neither deliquescent nor efflorescent. Their specific gravity is 2.226 at 63° . 100 of water dissolve 25 of this salt. When water saturated with it is set aside, crystals of the common sulphate are formed: it loses but little weight even at a red-heat: it is anhydrous and consists of

Soda	1 . .	32 . .	34.78
Sulphuric acid	$1\frac{1}{2}$. .	60 . .	65.22
<hr/>			
Anhydrous sesquisulphate of soda	1	92	100.00

A sesquisulphate of soda is obtained, according to Mitscherlich, by adding half an equivalent of oil of vitriol to sulphate of soda, and evaporating the solution till it attains the degree of concentration necessary for crystallization.

AMMONIO-SULPHATE OF SODA ($S+A+2S'$) is a double salt, formed by saturating the bisulphate with ammonia, (LINK, CRELL'S *Annals*,

1796, i.) or by dissolving the two sulphates in atomic proportions and crystallizing: it yields transparent prisms with rhombic bases, of a bitter taste. It consists of

Sulphate of soda	1	72	39·34
Sulphate of ammonia	1	57	31·15
Water	6	54	29·51
<hr/>			
Crystals of ammonio-sulphate of soda	1	183	100·00

SODIUM AND SELENIUM.—The seleniuret of sodium has not been examined.

SELENITE OF SODA is very soluble and difficultly crystallizable. It tastes like borax. It is insoluble in alcohol, and not deliquescent. *Biselenite of soda* is also very soluble: its solution when evaporated to the consistence of syrup forms clusters of radiated crystals. At a red-heat it fuses and gives off acid so as to become neutral. *Quadri-selenite of soda* yields radiated crystals by spontaneous evaporation. (BERZELIUS.)

SELENIATE OF SODA may be obtained by detonating a mixture of selenium and nitrate of soda. It is isomorphous with sulphate of soda, and follows the same law with regard to its solubility in water.

PHOSPHURET OF SODIUM ($so + p$) possesses the general properties of the corresponding compound of potassium.

HYPHOPHOSPHITE OF SODA ($S + \overline{p}$) is very soluble both in alcohol and water. (*Ann. de Ch. et Ph.*, ii. 142.) It may be obtained by mixing hypophosphite of lime with a slight excess of carbonate of soda, filtering, evaporating to dryness, and digesting in alcohol, which dissolves the hypophosphite, and which by very careful evaporation may be obtained in prismatic crystals which are very deliquescent, and when heated evolve phosphuretted hydrogen.

PHOSPHITE OF SODA ($S + \overline{p}$) forms rhombic crystals, very soluble in water and alcohol. (DULONG.) Insoluble in alcohol. (DUMAS.)

PHOSPHATE OF SODA. (RHOMBIC.) ($so + o$) + ($p + 2\frac{1}{2}o$) + $12(h + o)$. There is considerable difference of opinion as to the number and composition of the *phosphates of soda*. The salt commonly termed *phosphate of soda*, or *rhombic phosphate*, (the *sal perlatum* of some old writers,) is obtained by saturating the impure phosphoric acid, prepared from calcined bones by sulphuric acid (p. 484), with carbonate of soda: the liquor is filtered, evaporated, and set aside to crystallize. The crystals form most readily in an alkaline solution: they are oblique rhombic prisms, (BROOKE, *Ann. of Phil.*, 2nd series, vi. 286,) always alkaline to test-paper, superficially efflorescent, and soluble in about 4 parts of cold and 2 of hot water. This salt has a slightly saline and alkaline flavour, and has been used in medicine as an aperient under the name of *tasteless purging salt*. Its specific gravity is 1·33. Its concentrated aqueous solution often deposits silky crystals, but they are of the same composition as the other form. The crystals when heated fuse in their water of crystallization, and the salt afterwards runs into a clear glass, which becomes opaque on cooling: in this state it has the peculiarities of a *pyro-*

phosphate. It is deprived of half its alkali by hydrochloric acid, but not by acetic acid. The analyses of Berzelius and Mitscherlich, represent this salt, in its anhydrous state, as composed of

					Berzelius.	Mitscherlich.
Soda	1	32	47	..	46.52	47.37
Phosphoric acid	1	36	53	..	53.48	52.63
Anhydrous phosphate of soda	1	68	100		100.00	100.00

And in its ordinary crystalline form, as containing

					Berzelius.
Soda	1	32	18.2	..	17.67
Phosphoric acid	1	36	20.4	..	20.33
Water	12*	108	61.4	..	62.00
Rhombic phosphate of soda	1	176	100.0		100.00

When a solution of this phosphate is evaporated at a temperature of 90°, it crystallizes according to Clark (*BREWSTER'S Journal*, vii. 311,) in a modified form with only 8 atoms of water. When dropped into nitrate of silver, it forms a yellow precipitate.

SUBPHOSPHATE OF SODA. $\frac{1}{2}(SO + O) + (p + 2O) + 12(h + O)$.—When excess of caustic soda is added to a solution of the preceding salt, it yields on evaporation slender six-sided prisms which are permanent in the air, soluble in 5 parts of water at 60°, and undergo watery fusion at 170°. The solution of this salt absorbs carbonic acid, and is deprived of one-third of its alkali by the weakest acids. (*GRAHAM.*) This salt contains

Soda	$1\frac{1}{2}$	48	25.0
Phosphoric acid	1	36	18.8
Water	12	108	56.2
Crystals of subphosphate of soda	1	192	100.0

PYROPHOSPHATE OF SODA. $(SO + O) + (p + 2O) + 5(h + O)$.—When the rhombic phosphate of soda is heated to redness, so as to expel its water, and again dissolved and crystallized, it acquires a new prismatic crystalline form (*HAIDINGER, BREWSTER'S Journal*, vii. 314), and now instead of precipitating nitrate of silver yellow, as the rhombic salt does, it throws it down white. (See *Pyrophosphoric Acid*, p. 492.) According to Clark, it consists in this state of 1 atom of anhydrous phosphate and 5 atoms of water, the elements being,

Soda	1	32	28.3
Phosphoric acid	1	36	31.9
Water	5	45	39.8
Crystallized pyrophosphate of soda	1	113	100.0

BIPHOSPHATE OF SODA, CRYSTALLIZED. $(SO + O) + 2(p + O) + 4(h + O)$.—When phosphoric acid is added to a solution of rhombic phosphate of soda till it ceases to precipitate chloride of barium, it yields on evaporation very soluble crystals of an acid taste. They are generally in the form of right rhombic prisms, but sometimes in rectangular octoëdra. Their solution gives a yellow precipitate with nitrate of silver. They consist of—

* $12\frac{1}{2}$ according to *GRAHAM.*

Soda	1	32	22.86
Phosphoric acid	2	72	51.43
Water	4	36	25.71

Crystallized biphosphate of soda	1	140	100.00
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BIPYROPHOSPHATE OF SODA. $(SO + O) + 2(p + 2iO) + (h + o)$.—This salt is formed by the application of a graduated heat to the biphosphate of soda; its solution has an acid reaction, and does not crystallize. At a temperature of 500° , it becomes nearly anhydrous, and affords a solution *neutral* to test-paper; at a higher temperature, though short of a red-heat, it becomes anhydrous and appears to have lost its solubility in water; at least it is not affected at first when thrown in powder into boiling-water, but gradually dissolves by continued digestion, and passes into *metaphosphate*. (GRAHAM, *Phil. Trans.*, 1833, p. 275.) It consists of

Soda	1	32	23.3
Phosphoric acid	2	72	63.8
Water	1	9	7.9

Bipyrophosphate of soda	1	113	100.0
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METAPHOSPHATE OF SODA.—Graham thus designates an anhydrous biphosphate, $(SO + O) + 2(p + 2iO)$, obtained by heating the crystallized biphosphate, the ammonio-phosphate, or the bipyrophosphate of soda, to redness: "metaphosphate of soda fuses at a heat which does not exceed low redness, and on cooling forms a transparent glass, deliquescent in damp air, and very soluble in water, but insoluble in alcohol; its solution has a feeble acid reaction which can be negated by the addition of 4 per cent. of carbonate of soda. When evaporated, this solution does not give crystals, but dries into a transparent pellicle like gum, which retains at the temperature of the air somewhat more than a single equivalent of water. Added to neutral and not very dilute solutions of earthy and metallic salts, metaphosphate of soda throws down insoluble hydrated metaphosphates, of which the physical condition is remarkable; they are all soft solid or semifluid bodies, the metaphosphate of lime having the degree of fluidity of Venice turpentine."

AMMONIO-PHOSPHATE OF SODA exists in human urine, whence it was procured by the early chemists under the names of *microcosmic* and *fusible salt*. It may be formed by dissolving 5 parts of crystallized phosphate of soda with 2 of crystallized phosphate of ammonia, and evaporating; or, according to Graham, by heating together 6 or 7 parts of crystallized phosphate of soda, and 2 of water, till the whole is liquid, and then adding 1 part of powdered sal-ammoniac; chloride of sodium separates, and the solution, filtered and concentrated, affords the double phosphate in prismatic crystals; it is purified by a second crystallization. It forms transparent prisms, very fusible, and which at a red-heat lose water and ammonia, and leave biphosphate (metaphosphate) of soda, in the form of a transparent glass. They consist, according to Mitscherlich, of

Soda	1	32	15.2
Ammonia	1	17	8.0
Phosphoric acid	2	72	34.1
Water	10	90	42.7

Crystallized ammonio-phosphate of soda	1	211	100.0
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I have already stated Mr. Graham's views respecting the modifications of the phosphoric acid, and that, doubling the atom of phosphorus, he represents phosphoric acid by 1 equivalent of phosphorus and 5 of oxygen, $PO_5 = (\frac{1}{2}p + 5o)$ or $2(p + 2\frac{1}{2}o)$ of our equivalents. Consistently with his views of the constitution of the acids of phosphorus, and of the phosphates of soda, he represents the latter by the annexed formulæ, in which it will be seen that the atomic equivalents are doubled throughout, and that the water of the salts is considered partly as *constituent* water, belonging essentially to the salt, and partly as water of crystallization. Thus, if we set out with his *terhydrate of phosphoric acid* (p. 492), and add to it 1 atom of soda, only 1 atom of its constituent of water is displaced, and 2 are retained, and we obtain a tribasic salt, consisting of 1 atom of soda, and 2 of water, (as *bases*,) which is the *biphosphate of soda* of the annexed table. If we add 2 atoms of soda to the terhydrated phosphoric acid, (or a second atom of soda to the biphosphate,) we then displace another basic atom of water, and a tribasic salt is produced containing 2 atoms of soda and 1 of water, (as *bases*,) which is the common rhombic salt, or *crystallized phosphate of soda* of the table. A third atom of soda, added to the last salt, displaces the remaining atom of basic water, and a tribasic phosphate is formed, of which the whole 3 atoms of base are soda, and which is the *subphosphate of soda* of the annexed table; and this salt can unite with no more soda. The same three salts, Mr. Graham observes, may be formed by means of the tribasic phosphate of water in another manner. That acid hydrate decomposes chloride of sodium, but only to a certain extent, expelling hydrochloric acid, so as to acquire 1 of soda, and becomes $2HO, NaO + PO_5$, or the *biphosphate of soda*, (applying the old trivial

TABLE shewing the Composition of the *Phosphates* in reference to their basic or constituent Water (GRAHAM), and their Water of Crystallization.

GRAHAM.		BRANDE.	
		Formula.	Abbreviated Formula.
Crystallized phosphate of soda	$HO, 2 NaO, PO_5 + 24 HO$	$(so + o) + (p + 2\frac{1}{2}o) + 12\frac{1}{2}(h + o)$	$S + p' + 12\frac{1}{2}q$
Crystallized subphosphate of soda	$3 NaO, PO_5 + 24 HO$	$1\frac{1}{2}(s + o) + (p + 2\frac{1}{2}o) + 12(h + o)$	$1\frac{1}{2}S + p' + 12q$
Crystallized biphosphate of soda	$2 HO, NaO, PO_5 + 2 HO$	$(so + o) + 2(p + 2\frac{1}{2}o) + 4(h + o)$	$S + 2p' + 4q$
Crystallized pyrophosphate of soda	$2 NaO, PO_5 + 10 HO$	$(so + o) + (p + 2\frac{1}{2}o) + 5(h + o)$	$S + p' + 5q$
Bipyrophosphate of soda	HO, NaO, PO_5	$(so + o) + 2(p + 2\frac{1}{2}o) + (h + o)$	$S + 2p' + q$
Metaphosphate of soda	NaO, PO_5	$(s + o) + 2(p + 2\frac{1}{2}o)$	$S + 2p'$
Crystallized ammonio-phosphate of soda	$HO, NH_4O, NaO, PO_5 + 8 HO$	$(so + o) + (n + 3h) + 2(p + 2\frac{1}{2}o) + 10(h + o)$	$S + A + 2p' + 10q$

term.) The same acid hydrate applied to the carbonate or acetate of soda, can assume 2 atoms of soda, displacing twice as much of the weaker carbonic or acetic acids as of hydrochloric acid, and so becomes $\text{HO}, 2\text{NaO} + \text{PO}_5$, or the *common phosphate of soda*; and the same acid hydrate applied to the hydrate of soda, (caustic soda,) assumes 3 of soda and becomes $3\text{NaO} + \text{PO}_5$, or the *subphosphate of soda*. (See *Phosphate of Lead*, and *Phosphate of Silver*, in further reference to this subject: see also GRAHAM'S *Elements of Chemistry*, p. 350.)

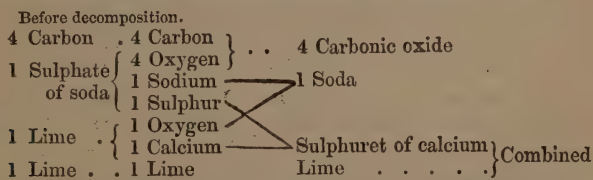
PHOSPHATE OF SODA AND POTASSA.—According to Mitscherlich there is a salt in which the atom of ammonia is replaced by one of potassa (potassa-phosphate of soda), but Mr. Graham says that it is the phosphate of soda with 14 atoms of water which has been mistaken for such a salt. (*Elements*, p. 476.)

CARBONATE OF SODA. ($\text{S} + \text{carb}$) or $\text{Na} \ddot{\text{C}}$.—This important salt was formerly obtained by the combustion of certain marine plants, the ashes of which afforded by lixiviation the impure alkali called *soda*. Two kinds of rough soda were known in the market, *barilla* and *kelp*; besides which, some *native carbonate of soda* was also imported. Barilla is the semi-fused ash of the *salsola soda*, which was cultivated upon the Mediterranean shore of Spain, in the vicinity of Alicant. (*Ann. de Chimie*, XLIX. 267.) Kelp consists of the ashes of sea-weeds, collected upon many of the rocky coasts of Britain, and burned in kilns, or merely in excavations made in the ground, and surrounded by stones. It seldom contains more than 5 per cent. of carbonated alkali, and about 24 tons of sea-weed are required to produce 1 ton of kelp. The best produce is from the hardest *fuci*, such as the *serratus*, *digitatus*, *nodosus*, and *vesiculosus*. (MACCULLOCH'S *Western Islands*, vol. i. p. 122.) The rough alkali, contaminated by chlorides of potassium and sodium, and other impurities, was to a certain extent purified by solution in a small portion of water, filtrating the solution, and evaporating it at a low heat: but kelp is now only important as a source of iodine (p. 371). At present the British market is supplied with carbonate of soda, obtained by the decomposition of sulphate of soda: it is manufactured to an enormous extent, at a very cheap rate, and of extreme purity; in many of the arts, soda has accordingly been substituted for potash. Small quantities of carbonate of soda are often found in an efflorescent form, upon walls containing lime and common salt: it also occurs in some mineral waters. A very pure carbonate of soda may be obtained by calcining acetate of soda at a red heat, and lixiviating the residue.

The following is an outline of the process by which carbonate of soda is now prepared. (GRAHAM, *Elements of Chemistry*. URE'S *Dictionary of Arts*. DUMAS, *Chimie app. aux Arts*.) 1. Sulphate of soda is prepared by the mutual action of equal weights of common salt and sulphuric acid diluted to the density 1.600: these are mixed in the chamber of a reverberating furnace and the disengaged hydrochloric acid suffered to escape by the chimney. 2. The sulphate of soda is ground up with an equal weight of chalk and half its weight of powdered coal, and this mixture is fused in a reverberating furnace, well stirred, and then raked out into an iron trough where it cools and solidifies. In this state it is called *ball-soda*, or *British barilla*, and contains about 22 per cent. of alkali. 3. This

is then broken up, placed in vats, and covered with warm water; in six hours the liquor is drawn, and the residue repeatedly washed till all soluble matters are extracted: the different liquors are then mixed and evaporated to dryness, by which a carbonate of soda is obtained, mixed with a little caustic soda and sulphuret of sodium. 4. This is further purified by mixing it with one-fourth its weight of sawdust, and exposing the mixture to a dull red heat, by which the sulphur is expelled and the caustic soda converted into carbonate. In this state it contains about 50 per cent. of alkali. 5. If crystallized carbonate of soda is required, this dry salt is dissolved in water, and when the solution has become clear, it is poured off, evaporated till a pellicle forms upon the surface, and then run into shallow iron vessels where it crystallizes. 6. The mother-liquors are boiled down to dryness and yield a less pure salt, containing about 30 per cent. of alkali which is used for soap and glass making.

In this process the sulphate of soda becomes sulphuret of sodium in consequence of the calcination with coal, and this sulphuret is converted into carbonate by the action of the chalk, sulphuret of calcium being also formed. Mr. Graham observes that this sulphuretted calcium would destroy the carbonate of soda if dissolved along with it in the lixiviation of the ball soda, but that being in combination with the lime, as an oxysulphuret of calcium, this does not happen; hence the necessity of excess of lime: he gives the following diagram in illustration of the process, assuming that charcoal is used instead of coal, and lime instead of carbonate of lime: the numbers denote equivalents.



The soda acquires carbonic acid, either from the carbonate of lime, or from the fuel.

The insoluble oxysulphuret of calcium in this process is known as *soda-waste*. It has, hitherto, says Mr. Graham, "been not merely valueless but troublesome to the manufacturer: at present an attempt is making to turn it to account as a source of sulphur." Mr. Phillips has suggested the use of sulphate of iron obtained by the oxidation of iron pyrites, as a substitute for the sulphuric acid in the above process, to convert the chloride of sodium into sulphate of soda; in this case sulphate of soda, oxide of iron, and a volatile chloride of iron, are the results; or the salts may be dissolved and the solution exposed to a low temperature, when sulphate of soda crystallizes and chloride of iron remains dissolved. Sulphate of magnesia has also been substituted in this process, for sulphate of iron.

Another mode of producing carbonate of soda, consists in the mutual decomposition which ensues when carbonate of ammonia and chloride of sodium are made to re-act upon each other in the humid way. For the following outline of this ingenious process, which has been patented by

Messrs. Dyer and Hemming, I am indebted to the latter:—"Mix common salt with an equivalent proportion of sesqui-carbonate of ammonia, and as much water as will dissolve the salt. Keep the ingredients in constant agitation for several hours; the result is a thick magma. Filter the liquid from the solid, and afterwards submit the solid to great pressure by an hydraulic press. The solid cake, which is chiefly bicarbonate of soda, is then to be heated in an iron retort till all the moisture, and one equivalent of carbonic acid, are expelled: it is now good soda-ash. The retorts are provided with pipes, communicating with a tank, in which the volatilized carbonate of ammonia is saved. The filtered and expressed liquors (which chiefly contain sal-ammoniac) are distilled with lime, and yield a solution of caustic ammonia. This is added to an equivalent proportion of common salt and agitated for several hours, during which a current of carbonic acid, obtained from ignited coke mixed with chalk, is forced through the mixture. The vats in which this operation is performed are rendered air tight, and the gas passes from one to another, and finally into a waste tub containing salt and water; the arrangement of the mixing vats being similar to that of a series of Woulfe's bottles. The carbonic acid converts the caustic ammonia into carbonate, which decomposes the salt as it is formed: the results are treated as before described. The chalk from which we obtain carbonic acid, furnishes the lime for the distilled liquors. We obtain our ammonia chiefly by distilling the ammoniacal liquor of coal gas with lime, and redistilling with a little more lime. By this mode we obtain a *very strong* solution of caustic ammonia, somewhat contaminated with sulphuretted hydrogen; this, however, is displaced by carbonic acid. It may be necessary to observe that we pass the carbonic acid through two waters to wash and cool it, and as it is indispensable that our mixtures should be kept *cool*, the water in the coolers is kept about one foot deeper than the column in our mixing vats, so that the gas enters under pressure, and by expanding cools the mixtures. As we have abundance of liquid ammonia, we propose to distil our filtered and expressed liquors *per se*. By this we soon separate any free and carbonate of ammonia; the residue is a solution of common salt and sal ammoniac. At a boiling heat the common salt, being much less soluble than the sal ammoniac, is taken out in the solid state and used again. The solution of sal ammoniac is boiled to dryness, and, resublimed in the usual way, furnishes an excellent article."

The primitive crystalline form of carbonate of soda is an oblique rhombic prism, the modifications of which have been described by Mr. Brooke (*Ann. of Phil.*, N. S., vi. 287). Its usual form is a rhombic octoëdron, the acute angles of which are truncated. Its sp. gr. is 1.62. It is soluble in twice its weight of water at 60°, and in less than its own weight at 212°. "The strongest solution that can be preserved at the temperature of the atmosphere has the specific gravity 1.26; but even this is liable to partial crystallization." (HENRY.) Its taste is strongly alkaline, and it greens vegetable blues. It fuses very readily in its water of crystallization, and on pouring off the fused salt, a portion of anhydrous carbonate remains. The fused salt congeals at about 90°. Exposed to a dry atmosphere the crystals effloresce, and gradually crumble down into a white powder: at a red-heat it loses the whole of its water.

In its anhydrous state it consists of

				Berzelius.	Dalton.
Soda	1	32	59.26	58.75	59.6
Carbonic acid	1	22	40.74	41.25	40.4
Anhydrous carbonate of soda	1	54	100.00	100.00	100.0

The perfect crystals, as they ordinarily occur, consist of

				Bergman.
Soda	1	32	22.22	20
Carbonic acid	1	22	15.28	16
Water	10	90	62.50	64
Crystals of carbonate of soda	1	144	100.00	100

When the crystals are formed at a temperature between 80° and 90° , they sometimes form large right rectangular prisms, terminated by a four-sided pyramid: these only contain 8 equivalents of water. A saturated solution of carbonate of soda, kept for a long time at 120° , deposited transparent prismatic crystals, harder than the common carbonate, and containing only 1 equivalent of water; and another variety, described by Mohs, contained $1\frac{1}{2}$ of water.

In the analysis of barilla, kelp, and other impure kinds of soda, to ascertain the relative proportion of soda, it may be useful to know that 100 parts of dilute nitric acid, specific gravity 1.36, will saturate 50 parts of dry carbonate of soda, which are equivalent to about 29 of pure soda; or 460 grains of dilute sulphuric acid, specific gravity 1.141, neutralize 100 grains of the dry carbonate. From either of these data, the quantity of real alkali in any sample of the rough salt may easily be calculated. But the method of ascertaining the proportion of soda, or of carbonate of soda, in these cases, by means of the *alkalimeter*, has already been described. (See *Alkalimetry*, p. 638.)

It has above been stated that, when excess of chlorine is passed into a solution of carbonate of potassa or of soda, carbonic acid is expelled and chlorides and chlorates formed: by peculiar management, however, chlorine may be combined with a solution of carbonate of soda, and the resulting combination has, from the uses made of it, and the name of its inventor, been termed *Labarraque's disinfecting liquid*. It is obtained as follows: 2800 grains of crystallized carbonate of soda are dissolved in 1.28 pints of water, and being put into a Woulfe's apparatus, the chlorine slowly evolved from a mixture of 967 grains of salt with 750 grains of black oxide of manganese, and 967 grains of sulphuric acid, previously diluted with 750 grains of water, is carefully passed into it. No carbonic acid is evolved, and a pale yellow liquid is the result; its taste is sharp, saline, and astringent, and it at first reddens, and then bleaches turmeric paper. It is but little changed by a boiling-heat, and gives out no chlorine. By careful evaporation, it furnishes crystals which produce the original liquid when redissolved; but exposed to the air, and suffered to evaporate spontaneously, the chlorine escapes, and crystals of carbonate of soda are obtained. (FARADAY, *Quarterly Journal*, N. S., vol. ii. p. 84.)

BICARBONATE OF SODA ($S+2CAR'$) is formed by passing carbonic acid through a strong solution of the carbonate: a granular or crystalline

powder is deposited, which, when carefully dried at common temperatures, consists of 1 atom of bicarbonate of soda, with, according to some 1 atom, according to others 2 atoms, of water. Both combinations may probably be formed. Mr. Graham represents this salt as a double carbonate of water and soda, by the formula $(q + car') + (S + car')$, or in his symbols $HO, CO_2 + NaO, CO_2$.

Bicarbonate of soda has a very slightly alkaline taste, and is much less soluble in water than the carbonate; requiring, according to Berthollet 8, according to Rose 13, of cold water. It loses carbonic acid if moistened and left in the vacuum of an air-pump, and the gas is also evolved when one part of the salt is boiled with four of water. In these cases the salt appears to be converted into a *sesquicarbonate*. (*Quarterly Journal*, xv. 383.) At a red-heat bicarbonate of soda loses its water, and half its acid, and becomes converted into dry carbonate of soda.

This salt, as well as the bicarbonate of potassa, may be obtained by treating their respective carbonates with carbonate of ammonia; pure ammonia is evolved and bicarbonates are formed. Bicarbonate of soda may also be obtained by condensing carbonic acid upon crystals of the carbonate; a portion of the water of the latter salt separates, and when the gas ceases to be absorbed, it is found converted into a porous and friable bicarbonate, which must be carefully dried at a low temperature, otherwise it loses a portion of its carbonic acid, and becomes a sesquicarbonate. The salt directed for pharmaceutical use is represented by Mr. Phillips as a sesquicarbonate, obtained by drying the bicarbonate "by a gentle heat." (*London Pharmacopæia*.) According to Graham, the bicarbonate of commerce generally contains 40 per cent. of soda, owing to the presence of neutral carbonate, in the state of protohydrate, which last salt may be separated by a small quantity of water.

In the manufacture of this bicarbonate for the purpose of commerce 160 lbs. of carbonate may be dissolved in 13 gallons of water, and carbonic acid thrown into the solution in a proper apparatus. The bicarbonate falls as it forms to the amount of about 50 lbs., and being separated from the solution may be conveniently dried by pressure in an hydraulic press. A fresh portion of carbonate is dissolved in the mother-liquor, and the operation repeated as before.

Regarded as containing 1 atom of water, the components of this salt are

Soda	1	32	37.6
Carbonic acid	2	44	52.6
Water	1	9	9.8
Bicarbonate of soda	1	85	100.0

SESQUICARBONATE OF SODA. $(S + 1\frac{1}{2}car')$.—A carbonate of soda occurs *native* in the Soda Lakes of Hungary, and in abundance in Africa, in the province of Gahena, near Fezzan. The natives call it *Trona*. It is found in hard striated crystalline masses, and is not altered by exposure to air: indeed, the walls of Cassar, a fort now in ruins, are said to have been built of it. A very productive soda lake also exists in South America, in Maracaybo, one of the provinces of Venezuela. Klaproth and Phillips have shown that it is a compound intermediate between the

carbonate and bicarbonate, (*Beiträge*, iii. 98, and *Quarterly Journal*, vii. 298,) consisting of

					Phillips.
Soda	1	32	38.5	}	78.2
Carbonic acid	1½	33	39.8		
Water	2	18	21.7		
Sesquicarbonate of soda	1	83	100.0		100.0

CYANURET OF SODIUM.—Sodium and cyanogen act with the same phenomena as potassium and cyanogen, and the resulting cyanurets resemble each other.

BORATE OF SODA. BORAX. (S+60'.)—This salt, which has been very long known, is imported chiefly from India, in an impure state, covered by a soapy matter, under the name of *Tincal*, *Pounxa*, or *Chrysocolla*; when purified, it is called *Borax*. It is also manufactured by combining soda with native boracic acid imported from the South of Italy. This process, as well as the methods of refining Indian and Chinese borax, are described by Dumas. (*Chim. App. aux Arts*, ii.) Borax crystallizes in irregular hexaëdral prisms, slightly efflorescent. Its taste is alkaline and styptic, and it has an alkaline reaction upon turmeric. It is soluble in 12 parts of cold and 2 of hot water. When heated it loses water of crystallization, and becomes a porous friable mass, called *calcined borax*. At a red-heat it runs into a transparent glass, which, by exposure to air, becomes opaque and pulverulent upon the surface. Its specific gravity in this state is 2.36.

Anhydrous borax consists of

					Arfwedson.
Soda	1	32	31.4	}	68.6
Boracic acid	1	68	68.6		
Anhydrous borate of soda	1	100	100.0		

and crystallized borax, of

					Kirwan.
Soda	1	32	16.84	}	34
Boracic acid	1	68	35.79		
Water	10	90	47.37		
Prismatic borate of soda	1	190	100.00		100

Sulphuric acid decomposes this salt, producing sulphate of soda and boracic acid (p. 580). It is also decomposed by nitric and hydrochloric acids, and by the greater number of the vegetable acids. It has a place in the *Pharmacopœia*. It is often used as a blow-pipe flux, vitrifying the greater number of the metallic oxides, and forming beads of different colours: violet with manganese; green with iron, chrome, and copper; blue with cobalt; and slightly yellow with some of the colourless oxides. This property of borax renders it also an useful ingredient in the pastes which are manufactured under the name of *artificial gems*. In the reduction of the metals by charcoal, borax is often useful as forming a medium through which the globules fall and collect into a button, being at the same time protected from the air. Alone, or mixed with phosphate of ammonia, or soda, borax is employed to render muslin and other arti-

cles of dress, as also paper, wood, and other materials, to a certain extent incombustible; this it does by covering them with a vitrifiable glaze by which the access of air is prevented. Borax is also used in the process of *soldering*; when, for instance, two surfaces of copper are to be soldered together they are scraped or rubbed clean, sprinkled with a mixture of powdered borax and solder-filings, and heated till the solder fuses so as to alloy with the copper and make a perfect joint: the borax not only prevents the contact of air, and consequent oxidation of the metals, but dissolves any oxide accidentally formed, and so retains the surfaces in that perfectly clean state which is requisite for their union.

OCTOËDRAL BORATE OF SODA.—This salt, discovered by Payen, contains 5 instead of 10 atoms of water: it is obtained by dissolving common borax in boiling water till the solution has a specific gravity 1.26; it is then allowed to cool slowly, and between the temperatures of 174° and 145° it deposits octoëdral crystals; below that temperature, the ordinary prismatic crystals are formed.

Octoëdral borax is harder than the prismatic; its specific gravity is 1.815; it has a brilliant conchoidal fracture, and is preferred for brazing and soldering; its equivalent is 145, that of prismatic borax being 190.

BOROFLUORIDE OF SODIUM is obtained by combining fluoride of sodium with fluoboric acid: it forms prismatic crystals of a bitter and sour taste, easily soluble in water, fusible and anhydrous. (BERZELIUS.)

SODIUM AND POTASSIUM form an *alloy*, which, if composed of one part of potassium and three of sodium, remains fluid at 32° . Equal parts of the metals form a brittle crystallizable alloy.

THE SALTS OF SODIUM are soluble in water. They are not precipitated either by pure or carbonated alkalis, or hydrosulphuret of ammonia, or tartaric acid, or ferrocyanuret of potassium; they produce no precipitate in solution of chloride of platinum, and do not convert sulphate of alumina into distinctly octoëdral alum. Potash and soda salts may also be distinguished as follows:—"Dip a fine clean platinum wire into the solution of the salt to be tested; dry it over a flame of alcohol burning in a small saucer; then put the wire into the blue part of the flame: if potassa, a rich purple or lilac tint is given; if soda, a bright yellow; these appearances are best seen in a dark corner: the yellow colour given by soda is more decided than the purple by potassa, so that smaller quantities of the former may be thus recognised. (CLARK.) Mr. A. Taylor informs me that oxalic acid gives a colour to flame resembling that given by potassa and its salts. When potassa or a salt of potassa is added to a globule of fused borax and oxide of nickel before the blowpipe they communicate to it a blue colour, which is not the case with soda or the salts of soda. But the best distinction between these two alkalis is found in the perfectly distinctive characters of their respective sulphates, carbonates, and nitrates, and more especially in the prismatic, efflorescent and fusible character of the sulphate soda,

§ III. LITHIUM.

In the analysis of a mineral found in the mines of Utö, in Sweden, in the year 1808. (*Ann. de Ch. et Ph.*, x.), called *petalite*, M. Arfwedson discovered between 5 and 6 *per cent.* of an alkaline substance, which was at first supposed to be soda; but, finding that it required for its neutralization a much larger quantity of acid than soda, he was led to doubt its identity with that alkali, and the further prosecution of his inquiries fully demonstrated that it possessed peculiar properties. The mineral called *triphane*, or *spodumene*, also affords the same substance, to the amount of nearly 9 *per cent.*, and it exists in *lepidolite*, in some varieties of *mica*, in *green tourmaline*, and, according to Berzelius, in the waters of Carlsbad, in Bohemia: the term *lithia*, deduced from its lapideous original (*λίθιος*, *lapideus*), has been applied to it.

The following is Arfwedson's mode of obtaining lithia from the *Petalite*: Reduce the mineral to a fine powder, and fuse it with about half its weight of potassa; dissolve the fused mass in hydrochloric acid, filter, and evaporate to dryness; digest the dry mass in alcohol; the only substance present, soluble in that liquid, is the *chloride of lithium*, which is taken up, and by a second solution and evaporation is obtained pure. It may be decomposed by digesting carbonate of silver in its aqueous solution, by which a carbonate of lithia is formed, decomposable by lime, in the way of the other alkaline carbonates.

Berzelius separates lithia from *spodumene* or from *petalite* as follows: One part of the mineral is reduced to a fine powder with about two parts of fluor-spar; this mixture is made into a thin paste with sulphuric acid, and heated in a silver crucible as long as acid vapours are given off, and ultimately to redness nearly; the dry mass is then digested in water, filtered, boiled with caustic ammonia to precipitate any alumina that may be present, filtered again, and evaporated to dryness: the dry mass, after having been heated to redness, to expel sulphate of ammonia, is pure *sulphate of lithia*, from the solution of which the lithia may be thrown down in the state of *carbonate*, by carbonate of ammonia.

Dumas directs as follows: Reduce the mineral containing lithia to fine powder, mix it with four parts of carbonate or nitrate of baryta, and expose it to a high heat in a platinum crucible for an hour and a half: a compact white mass is obtained, which is partially soluble in dilute hydrochloric acid; evaporate this solution till the chlorides remain dry: the silica may be separated by washing the residue in boiling water, filtering the liquor, and washing the filter; the silica remains upon the filter. The filtered liquor contains the chlorides of lithium, aluminum, barium, and iron; add to it a sufficiency of sulphuric acid to precipitate the barium and decompose the chlorides; saturate the excess of acid by ammonia, and add carbonate of ammonia to the neutralized solution, which precipitates alumina and oxide of iron. One filtration is sufficient to separate these precipitates, and the liquor then contains sulphate and hydrochlorate of ammonia, and sulphate of lithia; evaporate it to dryness, drive off the volatile salts, and pure sulphate of lithia remains. Dissolve the sulphate of lithia in water, and add a sufficiency of baryta water to precipitate the sulphuric acid; the lithia remains in solution and may be

obtained by evaporating the filtered liquor to dryness. Or the sulphate of lithia may be decomposed by acetate of baryta; filter, and evaporate the solution of acetate of lithia to dryness, heat the residue in a platinum crucible, and fused carbonate of lithia remains; powder and dissolve it in hot water, and boil it with hydrate of lime, by which it is decomposed, and on filtering, carbonate of lime remains, and a solution of pure lithia is obtained.

PROTOXIDE OF LITHIUM. LITHIA ($li + o$), L or \dot{L} , is a white caustic substance, and when submitted, in the state of hydrate, to the action of the Voltaic pile, it is decomposed with the same phenomena as potassa and soda; a brilliant white and highly combustible metallic substance is separated at the negative pole. The properties of this metal have not hitherto been investigated, in consequence of the difficulty of procuring any quantity of its oxide.

Hydrate of lithia is less soluble in water than potassa or soda; its solution tastes acrid like the other fixed alkalis. It acts powerfully on vegetable blues, converting them to green. It is sparingly soluble in alcohol. It does not deliquesce by exposure, but absorbs carbonic acid and becomes opaque: it affords no precipitate with chloride of platinum, in which it differs from potassa, but resembles soda. It attacks platinum in its pure and carbonated state, and hence must be fused in a silver crucible. When its salts are heated on platinum before the blow-pipe, they tinge the flame red. Its principal distinctive characters are found in its salts.

Direct experiments upon the composition of lithia are yet wanting. By calculation from the composition of the sulphate, as analyzed by Vauquelin, it would appear to contain about 55.2 lithium + 44.8 oxygen; by other experimentalists, nearly the same results have been admitted; so that the number 10 has been generally assumed as the equivalent of lithium; but from the analysis of some of its salts by M. Hermann, of Moscow (POGGEND. xv.), as also by C. Gmelin, it appears that its atomic weight does not exceed 8; or even according to Hermann, 6. So that taking Gmelin's results as the mean, lithia will consist of

Lithium	1	. . .	8	. . .	50
Oxygen	1	. . .	8	. . .	50
<hr/>					
Lithia	1		16		100

CHLORIDE OF LITHIUM. ($li + c$).—This compound is obtained by dissolving lithia or its carbonate in hydrochloric acid, evaporating the solution to dryness, and fusing it out of the contact of air: it is a white semi-transparent substance. It evidently differs from the chlorides of potassium and sodium, in being extremely deliquescent; in being soluble in alcohol; in being decomposed when strongly heated in the open air, when it loses chlorine, absorbs oxygen, and becomes highly alkaline; in being very difficultly crystallizable in cubes; and in tinging the flame of alcohol of a red colour. It probably consists of

					Hermann.	Gmelin.				
Lithium	. . .	1	. . .	8	. . .	18.18	. . .	14.66	. . .	18.43
Chlorine	. . .	1	. . .	36	. . .	81.82	. . .	85.34	. . .	81.57
<hr/>										
Chloride of lithium	1			44		100.00		100.00		100.00

IODIDE OF LITHIUM.—The action of *iodine* and *bromine* on lithium has not been investigated, nor has the iodide or bromide of lithium been obtained by the action of hydriodic or hydrobromic acid upon lithia or its carbonate.

FLUORIDE OF LITHIUM is very difficultly soluble. Its solution deposits small opaque crystals. (BERZELIUS.)

NITRATE OF LITHIA ($L + N'$) is a very soluble and extremely deliquescent salt, fusible and decomposed by heat; its taste is cooling; it crystallizes in rhombic and acicular prisms; and is soluble in alcohol. It consists of

Lithia . . .	1	. . .	16	. . .	22.8
Nitric acid .	1	. . .	54	. . .	77.2
Nitrate of lithia	1		70		100.0

SULPHURET OF LITHIUM.—The action of sulphur on lithium and lithia appears analogous to its action on potassium and potassa, but the compounds have not been precisely examined.

SULPHATE OF LITHIA ($L + S'$) crystallizes in small rectangular prisms, perfectly white, and possessed of much lustre. Their taste is saline, and their solubility intermediate between that of sulphate of potassa and sulphate of soda. The crystals contain no water, and when pure are difficult of fusion, but they fuse at a dull red heat, if a little sulphate of lime be added. Their solution occasions no change in solution of platinum, nor in tartaric acid. This salt consists of

				C. Gmelin.	Hermann.
Lithia . . .	1	. . .	16	. . .	27.94
Sulphuric acid	1	. . .	40	. . .	72.06
Sulphate of lithia	1		56		100

According to Gmelin, crystals of sulphate of lithia may be obtained which contain 1 equivalent of water, or 14.4 *per cent*.

BISULPHATE OF LITHIA ($L + 2S'$) has been described as crystallizing in hexangular tables; but Berzelius denies that it is a distinct salt: he, however, admits that sulphate of lithia forms larger crystals when the solution contains excess of acid.

PHOSPHATE OF LITHIA has been examined by Gmelin: it may be obtained by adding phosphoric acid to sulphate of lithia; no precipitate is at first formed, but on adding excess of ammonia, an insoluble *phosphate of lithia* falls. This property enables us to separate lithia from potassa and soda. The phosphate of lithia may be decomposed by dissolving it in acetic acid, and adding acetate of lead: *acetate of lithia* remains in solution.

BIPHOSPHATE OF LITHIA is obtained in small crystals by dissolving the phosphate in phosphoric acid.

AMMONIO-PHOSPHATE OF LITHIA falls in crystalline grains, when a mixed solution of a salt of lithia and phosphate of ammonia is evaporated; the phosphate must not be in excess, and the solutions should be concentrated, and the evaporation slow, lest the ammonia escape and the liquid

become sour. This salt resembles the ammonio-magnesian phosphate in appearance, and it is fusible and evolves ammonia; but when heated with nitrate of cobalt, it becomes blue, whereas the magnesian salt becomes red.

PHOSPHATE OF SODA AND LITHIA is obtained when a salt of lithia is mixed with phosphate of soda and evaporated to dryness. The solution at first becomes turbid; but the double salt is chiefly formed during the drying of the mass, which when digested in a little water leaves it in the form of a light white powder. It is insoluble in fluids containing phosphoric salts, very sparingly soluble in cold water, and somewhat more soluble in boiling water. This salt, after exposure to a red heat, contains 15·08 per cent. of lithia. It is so sparingly soluble in water that it may be resorted to for the discovery of small traces of lithia in solutions, which for this purpose must be mixed with carbonate of soda, evaporated to dryness, the residue heated red-hot and redissolved in water, by which all other salts precipitable by phosphoric acid are got rid of; *pure* phosphate of soda is then added to the solution, and it is evaporated to perfect dryness; when this residue is acted on by water, the double phosphate remains undissolved. In appearance it resembles phosphate of lime or magnesia, from which it may be distinguished as follows: fused with carbonate of soda upon platinum-foil it is transparent, but becomes turbid on cooling, whereas the earthy salts do not fuse in this way with the alkali; if the fusion be performed on charcoal, the fused double salt is absorbed, but the earthy salts remain upon the charcoal, the carbonate of soda only being absorbed by it. (BERZELIUS.)

CARBONATE OF LITHIA. ($L + car'$).—When a strong solution of carbonate of ammonia is added to sulphate of lithia, a white precipitate of *carbonate of lithia* is formed. According to Dumas, it is best formed by decomposing sulphate of lithia by acetate of baryta, and calcining the resulting acetate of lithia; the small remaining portions of carbonate of baryta and carbon are removed by digesting the pulverized acetate in boiling water and filtering; by slow evaporation a crust of very small prismatic crystals of carbonate of lithia separates.

Carbonate of lithia requires at least 100 parts of water at 60° for its solution, (very difficultly soluble, or according to some insoluble, in cold water.) It is insoluble in alcohol. It is fusible, alkaline, effervesces with acids, and absorbs carbonic acid from the air. A solution of this carbonate, containing only 1-1000th of its weight, acts strongly upon vegetable colours. It is decomposed by lime and baryta. It consists of

				C. Gmelin.	Hermann.
Lithia	1	16	42·11	45·54	39
Carbonic acid	1	22	57·39	54·46	61
Carbonate of lithia	1	38	100·00	100·00	100

BICARBONATE OF LITHIA.—Carbonate of lithia is slightly soluble in water impregnated with carbonic acid. It is said to occur in this state in some mineral waters in Bohemia. By spontaneous evaporation, the carbonate separates in the form of a crystalline crust.

BORATE OF LITHIA much resembles borate of soda: it is alkaline to tests.

CHARACTERS OF THE SALTS OF LITHIA.—It appears from the preceding statement, that lithia is distinguished from potassa and soda by its greater saturating power in respect to acids: that is, by its lower equivalent number; and by forming difficultly-soluble salts with phosphoric and carbonic acids. Chloride of lithium is highly deliquescent, and dissolves in strong alcohol, which enables us to separate it from the chlorides of potassium and of sodium. This solution burns with a purplish flame, and the same tint is communicated to the flame of the blowpipe when any salt of lithia is fused upon a thin slip of platinum-foil; they also corrode that metal, and leave a yellow spot at the point of action. Lithia is distinguished from the alkaline earths-by forming soluble salts with sulphuric and oxalic acids, and by the alkaline re-action of its carbonate upon vegetable colours. Its salts are not precipitated by ferrocyanuret of potassium, nor by infusion of galls, nor by chloride of platinum, nor by caustic potassa: the precipitate, by carbonate of ammonia, being carbonate of lithia, re-dissolves when the liquid is diluted and boiled.

§ IV. CALCIUM.

THE existence of *calcium*, as the metallic base of lime, was first demonstrated by Davy in 1808; he found that when lime was rendered electro-negative in contact with mercury, an amalgam was formed, which, by distillation, afforded a white metal: when this metal was exposed to air, and gently heated, it burned, and produced the *oxide of calcium*, or *lime*. Our knowledge of calcium, is almost limited to this single experiment, and it has never been obtained in sufficient quantity to ascertain its general properties: its *equivalent* as determined by indirect but very satisfactory evidence, to which we shall presently recur, may be considered as =20. (20·5, TURNER.)

OXIDE OF CALCIUM. LIME. QUICK LIME. (*cal* + *o*) or C, or Ca.—Lime may be obtained in a state of considerable purity by exposing powdered white marble to a white-heat for an hour, in an open crucible, which expels the carbonic acid. To obtain absolutely pure lime, white marble may be dissolved in dilute hydrochloric acid, a little caustic ammonia added to the solution, and filtered: carbonate of ammonia is then added, and the precipitate washed, dried, and exposed for a sufficient time to a white-heat. This exposure to heat must always take place in an open vessel, for in a close vessel, out of the contact of air, the decomposition of carbonate of lime is very imperfect: indeed, powdered marble may be kept for many hours at a red-heat, without losing any carbonic acid, provided air and moisture be carefully excluded, but when a current of air or steam is passed over it, they constitute a medium into which carbonic acid has a tendency to diffuse. (See p. 382 and 233; also GRAHAM'S *Elements*, p. 187.) To obtain lime perfectly free from all traces of carbonic acid, the carbonate should first be heated in an open vessel, the lime thus obtained converted into a *hydrate*, and this again heated: all carbonic acid is thus effectually expelled.

Pure lime is white, or of a very pale gray tint; it is acrid and caustic, and has a powerful alkaline reaction on the usual tests, its specific gravity is 2·3 (3·08, DUMAS); it is very difficult of fusion, but remarka-

bly promotes the fusion of some other oxides, and is therefore used in several metallurgic processes as a cheap and powerful flux. When quite pure it can only be fused in very minute particles by the oxygen blow-pipe, or by the Voltaic flame. When intensely heated, as, for instance, by the oxyhydrogen blowpipe, it is remarkable for its luminosity; and at this very high temperature a minute quantity is volatilized (p. 224). It is an essential ingredient in mortar and other cements used in building. Exposed to air it absorbs water and carbonic acid, and losing its causticity becomes partially converted into carbonate of lime; so that when used as a manure it should be ploughed into the soil as speedily as possible, and not left in heaps upon the surface.

From the concurrent testimony of different analysts, the number 28 is assumed as the equivalent of lime (28·5, TURNER); and as it is the *protoxide* of calcium, it consists of

				Berzelius.	Davy.
Calcium 1	. . . 20	. . . 71·4	. . . 71·91	. . . 72·8	
Oxygen 1	. . . 8	. . . 28·6	. . . 28·09	. . . 27·2	
Lime 1	28	100·0	100·00	100·0	

HYDRATE OF LIME. SLAKED LIME. (C + q.)—When a small quantity of water is poured upon lime, a great rise of temperature ensues from the solidification of a portion of the water, and a bulky white-powder is obtained, which is a *hydrate*. The rise of temperature is so great when large heaps of good lime are suddenly slaked, as to inflame gunpowder and scorch wood; it certainly exceeds 500°, and when the operation is performed in a dark place light is also evolved. (PELLETIER.)

Hydrate of lime may be obtained in a crystalline form by placing lime-water under the receiver of an air-pump, containing another vessel of sulphuric acid. The water is thus slowly evaporated, and imperfect six-sided crystals are formed. (GAY LUSSAC, *Ann. de Ch. et Ph.*, i. 334.) In composition these crystals resemble the pulverulent hydrate. Exposed to the air, they gradually crumble down into carbonate of lime. Hydrate of lime is a compound of

				Dalton.	Gay Lussac. Crystallised.
Lime 1	. . . 28	. . . 75·7	. . . 75	. . . 76·25	
Water 1	. . . 9	. . . 24·3	. . . 25	. . . 23·75	
Hydrate of lime 1	37	100·0	100	100·00	

LIME-WATER.—At a temperature of 60°, 750 parts of water are required for the solution of one part of lime. Boiling water, however, as Mr. Dalton first observed (*New System of Chem. Phil.*), does not dissolve so large a quantity; one part of lime requires, according to Phillips, 1280 parts of water at 212° for its solution (*Ann. of Phil.*, N. S., i. 107); and water at 32° has its solvent power much augmented, one part of lime being soluble in 656 of water at that temperature. When lime-water is boiled, a portion of the lime is therefore precipitated; or aggregated, according to Phillips, into small crystalline grains. The cause of this crystallization he refers “to the effect which heat sometimes produces, of increasing instead of diminishing the attraction of cohesion, where this attraction is associated with a tendency to crystallize. This crystalline attraction, increased by that of the lime for a definite portion of water, is then

greater than the attraction of the hydrate of lime for the water of solution, and the consequence is that crystals are formed." Lime-water is limpid and colourless; its taste is nauseous, acrid, and strongly alkaline, and although the quantity of lime which it contains is relatively small, its alkaline reaction upon tests is very marked; it powerfully reddens turmeric, and changes the blue of violets and cabbage-liquor to green. It is usually prepared by pouring warm water upon powdered lime, and allowing the mixture to cool in a close vessel; the clear part is then decanted from the remaining undissolved portion of lime. When lime-water is exposed to the air, a pellicle of carbonate of lime forms upon its surface, which, if broken, is succeeded by others, until the whole of the lime is thus separated in the form of an insoluble carbonate. Lime-water is used in medicine as an antacid. What is termed *milk or cream of lime* is merely hydrate of lime diffused through lime-water.

PEROXIDE OF CALCIUM. BINOXIDE OF CALCIUM. (*cal* + 2 *o*).—When oxygen is passed over heated lime, it is absorbed, and a *peroxide of calcium* is formed; its general properties resemble those of the binoxides of barium and strontium. A hydrated peroxide of calcium is thrown down in the form of small brilliant scales, according to Thenard, when lime-water is dropped into oxygenated water. Peroxide of calcium consists of

					Thenard.
Calcium	.	.	.	1 . . . 20 . .	55.5
Oxygen	.	.	.	2 . . . 16 . .	44.5
<hr/>					
Peroxide of calcium	1	.	.	36 . .	100.0

CHLORIDE OF CALCIUM. MURIATE OF LIME. (*cal* + *c*).—This compound occurs in sea-water and in some saline springs and mineral waters, when it is generally accompanied by traces of bromine and sometimes of iodine; it is produced artificially by heating lime in chlorine, in which case oxygen is evolved equal in volume to half that of the absorbed chlorine. It is also formed when carbonate of lime is decomposed by the action of hydrochloric acid, the resulting solution evaporated to dryness, and the residue exposed to a red heat in closed vessels. It has a strong attraction for water; it soon deliquesces when exposed to air, and becomes what used to be called *oil of lime*. Hence it is that fused chloride of calcium, broken into small pieces, is frequently employed to deprive gases of their aqueous vapour; but when thus used, its absorptive powers in regard to some gases must not be overlooked. Its taste is bitter and acrid. One part of water at 60°, dissolves four parts of this chloride; its solubility, however, is greatly influenced by temperature, for at 32° one part of water will not dissolve more than two of the salt, and at 212° it takes up nearly any quantity. It is copiously soluble in alcohol, and much heat is evolved during the solution. Ten parts of anhydrous alcohol dissolve seven of chloride of calcium at the boiling point, and the solution in cold weather affords crystals in rectangular scales, which are an *alcoate* containing about 60 per cent. of alcohol instead of water of crystallization. (GRAHAM.) When fused it acquires a phosphorescent property, as was first observed by Homberg, and hence it was termed *Homberg's phosphorus*. It is abundantly produced in the manufacture of carbonate of ammonia, from the decomposition of hydrochlorate of ammonia by lime,

and hence has sometimes been called *fixed sal-ammoniac*. (See the diagrams, pp. 427 and 533.) Chloride of calcium consists of

						Ure.
Calcium	. . .	1	. .	20	. .	35.7 . . 36.7
Chlorine	. . .	1	. .	36	. .	64.3 . . 63.3
		<hr/>		<hr/>		
Chloride of calcium	1			56		100.0 100.0

Pelletier says that when carbonic acid is passed through a solution of chloride of calcium, the whole becomes a hard solid mass. If sulphuric acid be poured into a strong solution of chloride of calcium, the whole congeals into a solid mass of sulphate of lime, and hydrochloric acid escapes.

HYDRATED CHLORIDE OF CALCIUM is obtained by evaporating the aqueous solution to the consistence of a thick syrup; on cooling, it concretes into a crystalline mass, which may be reduced to powder: in this state it is used in frigorific mixtures, to mix with snow (p. 169). By exposing a strong aqueous solution of chloride of calcium to a cold of 32° , it yields striated four-sided prisms, consisting of

Chloride of calcium	. . .	1	. .	56	. .	50.9
Water	6	. .	54	. .	49.1
		<hr/>		<hr/>		
Hydrated chloride of calcium	1			110		100.0

OXYCHLORIDE OF CALCIUM.—When hydrate of lime is boiled in a solution of chloride of calcium, it is dissolved, and if the solution be filtered while hot, it deposits flat prismatic crystals which contain 49 per cent. of water, and which are decomposed both by water and alcohol. These crystals are composed of 3 equivalents of lime, 1 of chloride of calcium, and 15 of water.

AMMONIO-CHLORIDE OF CALCIUM.—Faraday has shown (*Quart. Journ.*, v. 74) that chloride of calcium absorbs large quantities of ammoniacal gas, during which it swells, cracks, splits in all directions, and at last crumbles down into a white powder. Exposed to the atmosphere it deliquesces less rapidly than the original chloride. Thrown into water it dissolves, forming a strong alkaline solution. Heated, it gives off ammonia, and the chloride remains unchanged. Immersed into chlorine, the ammonia burns off spontaneously with a pale-yellow flame. Faraday found that 19 grains of this compound gave off 19.4 cubic inches of ammonia; it probably, therefore, consists of

Chloride of calcium	1	. .	56	. .	76.7
Ammonia	1	. .	17	. .	23.3
		<hr/>		<hr/>		
Ammonio-chloride of calcium	1			73		100.0

CHLORIDE OF LIME. OXYMURIATE OF LIME.—This compound is abundantly employed as a bleaching material; it was first manufactured by the late Mr. Tennant, of Glasgow, who obtained a patent for it in 1799; it was made by passing chlorine into chambers containing hydrate of lime in fine powder, by which the gas is copiously absorbed, care being taken to suppress the extrication of heat. An account of the apparatus and machinery employed by the wholesale makers of this article, together with

many valuable remarks upon its composition and analysis, will be found in URE'S *Dictionary of Arts and Manufactures*. It is a dry white powder, smelling feebly of chlorine, and having an acrid taste: it is partially soluble in water, and the solution, which is used under the name of *bleaching liquor*, contains both chlorine and lime. Exposed to air it slowly evolves chlorine and absorbs carbonic acid; ultimately some chloride of calcium is formed, and it deliquesces. When heated, it gives off oxygen, and chloride of calcium results, an experiment which shows the superior attraction of calcium for chlorine as compared with oxygen, the latter being expelled from the lime.

The solution obtained by digesting bleaching powder in distilled water has a strong alkaline reaction upon most of the usual tests, and its bleaching power is only slowly developed unless some acid be added, when it is powerful and immediate: thus it is that the calico printers produce white figures upon coloured ground by printing the pattern intended to be brought out upon the coloured calico, in citric or tartaric acid thickened with starch or gum; the goods are then rapidly wound through a properly adjusted solution of chloride of lime, and the bleaching power only shows itself where the acid pattern had been previously applied; in the same way a solution of the chloride may be coloured blue by litmus, or green by red cabbage, or brown by turmeric, and on the addition of a few drops of acid the colour immediately disappears. By exposure to air the absorption of carbonic acid effects the same change, and the evolution of that acid in respiration is well shown by tinging a weak solution of chloride of lime blue by litmus, and then breathing through it by means of a tube, when the blue colour gradually disappears; an illustration, for which I am indebted to Mr. Alfred Taylor, of Guy's Hospital.

Dr. Ure has contrived an instrument for the speedy analysis of bleaching powder for the purposes of the artist, by which the quantity of chlorine in any given sample may be determined. (*Quarterly Journal*, xiii. 21.) "It consists of a glass tube, of about five cubic inches capacity, shaped as in the adjoining figure, and graduated into cubic inches and tenths. It is to be closed at top with a brass screw cap, and, at its recurved end below, with a good cork. Pour mercury into the upper orifice, till the tube be nearly full, leaving merely space to insert ten grains of the bleaching-powder, made into a pellet-form with a drop of water. Screw in the cap-plug rendered air-tight by leather. Remove now the cork from the lower end, (also full of mercury,) and replace a little of the liquid metal by dilute hydrochloric acid (specific gravity 1.1). By dexterous inclination of the instrument, the acid is made to flow up through the mercury. Instantly on its coming into contact with the pellet, the chlorine is disengaged, the mercury flows out into a basin ready to receive it, while the resulting film of muriate of lime protects the surface of the metal almost completely from the gas. With an apparatus of this



kind, which indeed is the same as that which I have long used for analyzing limestones and marbles, I get good accordances with the results derived from the loss of weight suffered by a like quantity of the chloride, when it is dissolved in dilute hydrochloric acid. Since a cubic inch of chlorine may be estimated in round numbers at $\frac{3}{4}$ of a grain, we may expect 10 grains of bleaching-powder to yield from 3 to 4 cubic inches of that gas, or by weight from 20 to 30 per cent., a wide range of power, which it is well worth the bleacher's or paper-maker's while to ascertain. If carbonic acid be suspected, we need only agitate the mercury through the gas, adding some of the metal from time to time as the absorption proceeds. The carbonic acid will remain uncondensed at the top, and may be estimated in the usual way."

Another mode of determining the commercial value of chloride of lime, consists in ascertaining its bleaching power by its effect upon a standard solution of indigo; directions for this purpose have been drawn up by Gay Lussac (*Ann. of Phil.*, xxiv. 218). Morin (*Ann. de Ch. et Ph.*, xxxvii. 142) tests it by solution of protochloride of manganese, determining its proportion of chlorine by the quantity of peroxide of manganese which it throws down; but the free lime present seriously interferes with the practical application of this test.

The composition of bleaching powder has been variously stated. Dalton (*Ann. of Phil.*, i. 15, and ii. 6) considers it as a *hydrated sub-chloride of lime*, containing 2 proportionals of lime and 1 of chlorine; and the same opinion is adopted by Thomson (*Ann. of Phil.*, xv. 401), and by Welter (*Ann. de Ch. et Ph.*, vii. 383). Dr. Ure, however, shows in the paper already quoted, that the quantity of chlorine absorbed is variable; he analyzed a specimen of good commercial bleaching powder, and found it composed of 46 lime, 23 chlorine, and 31 water: a specimen prepared by himself with pure hydrate of lime contained 45.40 lime, 40.32 chlorine, and 14.28 water; and he found the condensation of chlorine to vary with the pressure, the degree of exposure, and the quantity of water present. Upon the whole, it is not improbable that bleaching powder consists of a chloride of lime, containing 1 proportional of chlorine and 1 of lime, mixed with a varying proportion of hydrate of lime; and that when water acts upon the compound the solution contains a chloride of lime. Berzelius regards bleaching powder as a compound of chloride of calcium and *chlorite* of lime, and this opinion is said to be sanctioned by Balard's researches already quoted (p. 367), but if chlorite or hypochlorite of lime were formed by the action of chlorine upon pulverulent hydrate of lime, a large proportion of chloride of calcium must at the same time be produced, and we have no evidence of the existence of more than a trace of chloride of calcium in well-made bleaching powder. A specimen of chloride of lime of the best quality usually sold in London, consisted of 1 equivalent of chlorine, 2 of lime, and 2 of water. More lately this subject has been studied by Millon (*Jour. de Pharm.*, September, 1839), but without any important practical results; he, however, finds that many of the precipitates formed in metallic solutions by the addition of a solution of chloride of lime, consist of 1 equivalent of the metallic oxide combined with 1 of chlorine; as if, therefore, setting out with the binoxide of a metal, 1 equivalent of oxygen had been replaced by 1 of chlorine.

CHLORATE OF LIME ($C + c'$) is a very soluble deliquescent salt of a sharp bitterish taste, difficultly crystallizable, and soluble in alcohol. During its solution upon the tongue, or in water, it produces cold. It is most easily formed by dissolving carbonate of lime in chloric acid. Exposed to heat, oxygen is evolved, and a chloride remains. From Chenevix's analysis the crystals probably contain 2 atoms of water.

IODIDE OF CALCIUM ($cal + i$) is obtained by dissolving carbonate of lime in hydriodic acid, evaporating to dryness, and heating the residue in a close vessel till it fuses; it may also be obtained by digesting hydrate of lime with protiodide of iron: it is a deliquescent gray substance, which, heated in the air, absorbs oxygen and evolves iodine.

Dissolved in water and slowly evaporated, it furnishes deliquescent crystals, usually called *hydriodate of lime*; they are composed of the iodide and water. The iodide consists of

Calcium	1	20	13.3
Iodine	1	126	86.2
<hr/>			
Iodide of calcium	1	146	100.0

IODATE OF LIME. ($C + i'$).—This salt is formed by dissolving carbonate of lime in iodic acid; it also gradually crystallizes out of a mixed solution of iodate of potassa and chloride of calcium: it forms small prismatic crystals soluble in 5 of cold and 1 of boiling water, and containing 3 *per cent.* of water. (GAY LUSSAC, *Ann. de Chimie*, vol. xci., p. 84.)

BROMIDE OF CALCIUM ($cal + b$) was obtained by M. Henry by digesting hydrate of lime in a solution of protobromide of iron; it forms deliquescent acicules soluble in alcohol and water; it fuses and is partially decomposed when heated in open vessels.

BROMATE OF LIME ($C + b'$) has not been examined.

FLUORIDE OF CALCIUM. FLUOR-SPAR. ($cal + f$).—This compound may be produced artificially by saturating dilute hydrofluoric acid with newly-precipitated and moist carbonate of lime, and may thus easily be collected, and dried in the form of white powder. If obtained by precipitating a neutral salt of lime with a soluble fluoride, it forms a gelatinous mass, the precipitation of which is accelerated by the addition of caustic ammonia.

Native fluoride of calcium, or *fluor-spar*, is a mineral found in many parts of the world, but in great beauty and abundance in England, and especially in Derbyshire, where it is commonly called *blue John*. It is usually found in cubic crystals, which may easily be cleaved into octoëdra, and tetraëdra (p. 124). Its colours are extremely various. Its specific gravity = 3. It phosphoresces when exposed to a heat a little below redness (p. 217), and at a red heat it fuses: it is sometimes used as a flux for promoting the fusion of other minerals, hence its German name *Fluspath*, and the English *Fluor*. It generally occurs in veins; in the Odin mine at Castleton, in Derbyshire, it is found in detached masses, from an inch to more than a foot in thickness; their structure is divergent, and the colours, which are various, disposed in concentric bands. It is the

only variety which admits of being turned in the lathe into vases and other ornamental articles. *Compact fluor* is a scarce variety: the finest specimens come from the Hartz. A third variety is *chlorophane*, so called from the beautiful pale-green light which it exhibits when heated. The nature of the colouring-matter of blue and green fluor-spar is not exactly understood. It is liable to fade, and the blue varieties become red and brown by heat.

Fluoride of calcium exists, according to Berzelius, in bones, urine, and the enamel of the teeth, in the human subject; he also found it in minute quantities in some of the Carlsbad waters.

Pure fluoride of calcium is not decomposed by cold sulphuric acid, but forms with it a transparent viscid mixture. At a temperature of about 100° its decomposition begins, sulphate of lime forms, hydrofluoric acid is evolved, and the mixture grows opaque. If the fluor-spar contain silica, then sulphuric acid immediately acts upon it, evolving silicofluoric acid. Concentrated hydrochloric and nitric acids dissolve fluoride of calcium without decomposition, and become milky when diluted; but it is doubtful whether such solutions are formed when the fluoride is perfectly pure. It is scarcely soluble in hydrofluoric acid. Fused with carbonate of potassa, carbonate of lime and fluoride of potassium are produced. It is now generally admitted to be a binary compound of calcium and fluorine, consisting of

Calcium	1	20	52.6	53.313
Fluorine	1	18	47.4	46.637
Fluoride of calcium	1	38	100.0	100.000

NITRATE OF LIME. ($C + n'$).—This is a deliquescent salt, soluble in one-fourth its weight of water at 60° . It is found in old plaster and mortar, from the washing of which, nitre is procured by the addition of carbonate of potassa. It sometimes occurs in spring water; I have detected it in several samples sent to me for analysis by the Directors of the South-Western Railway, and elsewhere in the vicinity of London. Berzelius mentions it as accompanying nitrate of magnesia, in the well-waters of Stockholm.

The production of this salt in artificial nitre-beds has already been adverted to (p. 620). It may be crystallized, by very slow evaporation, in six-sided prisms, containing according to Bergman about 25 *per cent.* of water; but when obtained from a solution evaporated very low, and set aside in the cold, it appears in the form of groups of acicular crystals. It is soluble in an equal weight of boiling alcohol. When exposed to a moderate heat, it undergoes watery fusion; the water then evaporates and the salt fuses; on cooling it concretes into a semi-transparent phosphorescent substance, called from the discoverer of this property *Balduin's phosphorus*. (BIRCH'S *History of the R. S.*, iii. 328.) At a red heat it is decomposed; its acid is dissipated, and pure lime remains. Anhydrous nitrate of lime consists of

				Wenzel.
Lime	1	28	34.1	33.8
Nitric acid . .	1	54	65.9	66.2
Nitrate of lime	1	82	100.0	100.0

SULPHURET OF CALCIUM ($cal + s$) is formed by passing sulphuretted hydrogen, or the vapour of sulphuret of carbon, over red-hot lime. It is also formed by the action of charcoal or of hydrogen upon *sulphate of lime* at a red heat. It is of a reddish tint, slowly acted upon by water, forming a colourless solution of an hepatic and alkaline taste. When freshly prepared it is phosphorescent in a dark place, as was first observed by Canton. When its solution is carefully evaporated in vacuo it deposits small cubic crystals.

HYDROSULPHURET OF LIME ($cal + o$) + ($s + h$) is obtained by passing sulphuretted hydrogen through a mixture of quick-lime and water. The solution has an hepatic, acrid, and bitter taste, but it yields no crystals of hydrosulphuret; for when evaporated, sulphuretted hydrogen escapes, and crystals of sulphuret of calcium are then deposited.

When three parts of slaked lime and one of sulphur are boiled in twenty parts of water, and the solution allowed to cool upon the sediment, crystals are formed, which may be dried by exposure to the absorbent power of a large surface of sulphuric acid, placed under an exhausted receiver. Their form is that of quadrilateral prisms, with dièdral summits. They are sparingly soluble in cold water, the solution having a yellow colour, and an acrid, bitter, and sulphurous taste. They consist, according to Herschel (*Edin. Phil. Journ.*, i. 11), of

	Herschel.			
Lime	2	56	44.8	42.9
Sulphur	2	32	25.6	26.0
Hydrogen	1	1	0.8	0.6
Water	4	36	28.8	30.5
	<hr/>	<hr/>	<hr/>	<hr/>
	1	125	100.0	100.0

So that, excluding water, these crystals contain 2 atoms of lime and 1 atom of bisulphuret of hydrogen. They are generally represented as a bisulphuret of calcium, but such is not the result of Herschel's analysis.

PENTASULPHURET OF CALCIUM. ($cal + 5s$).—When the protosulphuret of calcium and sulphur are boiled together in water the sulphur continues to be dissolved till the lime has combined with 5 equivalents of it. A similar persulphuret is also formed when lime and excess of sulphur are boiled together with water, but in this case hyposulphite of lime and a portion of bisulphuret of calcium (Herschel's salt?) are also formed. (BERZELIUS.) Persulphuret of lime was proposed many years ago in Ireland as a substitute for potash ley in bleaching.

HYPOSULPHITE OF LIME. ($C + s$).—When sulphurous acid is ground in a mortar with crystals of Herschel's hydrosulphuret it loses its odour, and when filtered it is found to be a solution of *hyposulphite of lime*. By passing sulphurous acid through an aqueous solution of sulphuret of calcium, the same product is obtained; and if the solution be filtered and evaporated, at a temperature not exceeding 140° , it furnishes hexagonal crystals: the temperature of ebullition decomposes it. The crystals are little altered by air, very soluble in water, and insoluble in alcohol. They consist of

			Herschel.
Lime	1	28	21·8
Hyposulphurous acid	1	48	36·8
Water	6	54	41·4
Crystals of hyposulphite of lime	1	130	100·0

This salt has lately been employed as a means of removing the salts of silver from photogenic drawings, so as to render them permanent when exposed to light (see SILVER). Mr. Alfred Taylor, in his paper *On the Art of Photogenic Drawing*, directs its preparation for this purpose as follows:—

One ounce of sublimed sulphur is to be mixed with one ounce and a half of lime, previously slaked by the addition of hot water, and the mixture put into a clean earthen vessel. Three quarts of water are added, and the whole is to be boiled for two hours. The clear liquid may then be filtered off into several wide basins or dishes, and allowed to remain freely exposed to air. (The residue on the filter may, if required, be boiled with more slaked lime and water, until it ceases to yield a yellow coloured liquid.) When first made, the liquor is of a rich orange colour, but a scaly semi-crystalline crust soon forms on its surface; this must be broken down as often as it is produced, and the liquid be exposed to air until it has become quite colourless. The time required for this, varies according to the depth of the colour, and the quantity of persulphuret of calcium present in it. If weak, the change is complete in three or four days; if strong, the whole of the colour will not be lost until after the lapse of three or four weeks. The change is always accelerated by diluting the liquid; but this must not be carried too far. When colourless, the liquid, which is a solution of hyposulphite of lime, may be filtered off, and it is now fit for use. The scaly residue left on the filter, digested in cold water, will yield more of the hyposulphite.

SULPHITE OF LIME ($C+S$) is formed by passing sulphurous acid into a mixture of lime and warm water, or by mixing the solutions of chloride of calcium and sulphite of potassa. It is a white powder of a slightly sulphurous taste; it requires about 800 parts of water at 60° for its solution: it is rendered soluble by excess of sulphurous acid, and then separates in hexangular prismatic crystals, of difficult solubility, efflorescent, and passing into sulphate of lime by exposure to air. When heated this salt is converted into sulphuret of calcium and sulphate of lime. It consists of

Lime	1	28	46·7
Sulphurous acid	1	32	53·3
Sulphite of lime	1	60	100·0

HYOSULPHATE OF LIME. ($C+S'$).—This salt is formed by decomposing hyposulphate of manganese by lime, filtering, and evaporating the solution; it forms groups of transparent tabular crystals, permanent in the air, soluble in 0·8 of water at 212° , and in 2·46 of water at 60° , and insoluble in alcohol. (HEEREN, POGGEND. vii. 178.) The crystals consist of

Lime	1	23	20·6
Hyposulphuric acid	1	72	52·9
Water	4	36	26·5
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Crystals of hyposulphate of lime	1	136	100·0

SULPHATE OF LIME ($C + S'$) occurs native in *selenite*, *gypsum*, *plaster-stone*, &c. It is easily formed artificially, by dropping sulphuric acid upon lime, in which case there is great evolution of heat; or by decomposing a solution of chloride of calcium, or any of the soluble salts of lime, by sulphuric acid or by a soluble sulphate. When thrown down from its solutions, or in any way slowly deposited, it generally forms minute silky crystals soluble in 350 parts of water. When these, or the *native crystallized sulphate*, are exposed to a heat of from 4 to 500°, they lose water, and fall into a white powder (*plaster of Paris*), which, made into a paste with water, soon solidifies; and when in large quantity, with very sensible increase of temperature: hence its use in taking casts for busts, figures, and ornaments: it is also the basis of stucco and scagliola or artificial marble, which is made by mixing plaster of Paris, coloured in various ways, with size and water; when it has indurated, its surface is polished. Exposed to a red heat, but short of its fusing-point, it loses this property of recombining with water. Anhydrous sulphate of lime requires about 500 parts of water at 60°, and 450 parts at 212°, for its solution: or, according to Berzelius, it is equally soluble in cold and hot water, 1 part of the salt being soluble in 462 of water; according to Mr. Paul (*Phil. Mag.*, xv. 63), if this solution be saturated by pressure with hydrogen, the sulphate in about six months is converted into a sulphuret. As sulphate of lime is more soluble in water than pure lime, sulphuric acid affords no precipitate when added to *lime-water*. Nearly all spring and river water contains this salt, and in those waters which are called *hard* it is abundant: it gives to them a slightly nauseous taste, and renders them unfit for washing and for culinary use. At a very high temperature sulphate of lime is fusible, but suffers no decomposition; heated with charcoal it is converted into a sulphuret of calcium. It dissolves without decomposition in dilute nitric and hydrochloric acids, and separates from these solutions when concentrated, in long silky or transparent crystals. It is decomposed by the alkaline carbonates. Sulphate of lime is sometimes employed as a manure, and, when sprinkled over the land in small quantity, is said to improve certain soils, especially for the growth of clover: it may also be useful as a chemical agent. Anhydrous sulphate of lime consists of

Lime	1	28	41·2	Wenzel. 40·2	Bergman. 41
Sulphuric acid	1	40	53·8	59·8	59
<hr/>					
Sulphate of lime	1	68	100·0	100·0	100

And the native crystallized sulphate of lime consists of

Anhydrous sulphate of lime	1	68	79	Klaproth. 73·5	Bergman. 78
Water	2	18	21	21·5	22
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Crystallized sulphate of lime	1	86	100	100·0	100

Native Sulphate of Lime occurs in various forms. The *crystallized* or *hydrus* variety ($C + S^{1+2}Q$) is usually called *selenite**; the fibrous and earthy, *gypsum*†; and the granular or massive, *alabaster*‡. The primitive form of selenite is a rhomboidal prism of $113^{\circ} 8'$ and $66^{\circ} 52'$. The crystals are commonly transparent, of a specific gravity of 2.32, and of various colours; softer than native carbonate of lime, and yield very easily to the nail. They are often disseminated in argillaceous strata. It occurs in Cumberland at Alston, and in Oxfordshire at Shotover Hill, where it is accompanied by shells and pyrites, and appears to have resulted from their mutual decomposition. A beautiful fibrous variety, called *satin gypsum*, is found in Derbyshire, applicable to ornamental purposes, such as beads, broaches, &c. *Massive and granular gypsum* is found in this country in the red marl or new red sandstone accompanying the salt-deposits in Cheshire. It abounds in the tertiary strata of Montmartre, near Paris, and contains organic remains; sometimes it forms entire hills. In the Tyrolese, Swiss, and Italian Alps, it is found upon the primitive rocks, often of the purest white, especially at Montier, near Mont Blanc, and near the summit of Mont Cenis. It is turned by the lathe, and sculptured into a variety of beautiful forms, more especially by the Florentine artists. Columns for interior architecture are sometimes formed of it, as may be seen in the hall of Keddleston-house in Derbyshire.

There is a variety of sulphate of lime, which has been called *anhydrous gypsum*, or *anhydrite*, in reference to its containing no water. It is harder and denser than selenite, its specific gravity being 2.96: it sometimes contains common salt, and is then called *muriacite*. It is rarely crystallized, generally massive and lamellar, and susceptible of division into rectangular prisms. It has been found in Derbyshire and Nottinghamshire of a pale-blue tint; sometimes it is pink or reddish, and often white. It has also been found at Vulpino in Italy, and hence called *Vulpinite*. The statuariers of Bergamo and Milan employ it, and artists know it by the name of *Marbre di Bergamo*. A compound of sulphate of lime and sulphate of soda is found in the salt-mines of New Castile, which mineralogists have described under the name of *Glauberite*, and which probably might be formed artificially by fusing the two salts.

PHOSPHURET OF CALCIUM. (*cal+p.*)—By passing the vapour of phosphorus over lime heated to dull redness a brown compound is produced, which rapidly decomposes water with the evolution of phosphuretted hydrogen gas, and which consists of phosphuret of calcium and phosphate of lime; the oxygen of the lime at this temperature converts a portion of the phosphorus into phosphoric acid, and the evolved calcium combines with another portion of phosphorus to form phosphuret of calcium. *Hydrophosphuret* and *hypophosphite of lime* are formed by its action upon water, phosphuretted hydrogen gas escapes, and a phosphate of lime precipitates. When dilute hydrochloric acid is poured upon

* From $\sigma\epsilon\lambda\eta\nu\eta$, the moon, in reference to its soft lustre.

† From $\gamma\eta$, earth, and $\epsilon\psi\epsilon\omega$, to concoct: formed, or concocted in the earth.

‡ An ancient term applied to vases or boxes, for containing perfumes: perhaps from *a*, privative, and $\lambda\alpha\sigma\omega$, a handle, as opposed to vessels with handles.

this phosphuret, abundance of *phosphuretted hydrogen* is also liberated (p. 499).

The usual process for obtaining phosphuret of calcium is the following:—Select a green-glass or porcelain tube, closed at one end, and about eighteen inches long, and one inch diameter, and carefully cover it with a clay lute containing a very little borax. Put an ounce of phosphorus broken into small pieces into the lower end, and fill it up with pieces of clean quick-lime, about the size of large peas: place it in an inclined position in a furnace, so that the end containing the phosphorus may protrude, while the upper part of the tube is heating; then slowly draw the cool part into the fire, by which the phosphorus will be volatilized, and, passing into the hot lime, convert a portion of it into phosphuret. Care should be taken that no considerable portion of phosphorus escapes and burns away at the open end of the tube, which, after the process, should be corked and suffered to cool. Its contents may then be shaken upon a sheet of paper, and the brown pieces picked out, and carefully preserved in a well-stopped phial; the white pieces, or those which are only pale-brown, must be rejected. The success of this operation depends upon the skilful management of the temperature, and the difficulty of heating the whole of the lime up to a proper point, which should be short of a red heat; for if the temperature be insufficient, no combination ensues; and if too high, the compound is again decomposed, phosphorus evolved, and lime remains. According to Berzelius, phosphuret of lime is best obtained by heating pieces of lime in a long necked matrass over the flame of a spirit lamp and dropping phosphorus upon them. When the compound is perfect it is reddish brown or chocolate coloured; when breathed on or moistened it exhales a very strong and diffusive alliaceous odour, which it is difficult to get rid of; it heats and even burns if touched with damp hands, and when dropped into water the action is immediate and often violent, and the evolution of phosphuretted hydrogen continues for some time.

HYPOPHOSPHITE OF LIME may be obtained by boiling phosphorus in thin cream of lime, filtering off the solution, and passing carbonic acid through it, to separate excess of lime. The clear solution evaporated in vacuo furnishes four-sided rectangular prismatic crystals of the hypophosphite, which are nearly equally soluble in hot and cold water, and quite insoluble in alcohol: they contain from 18 to 22 per cent. of water of crystallization. At a red heat in air they are converted into biphosphate of lime; also by the action of nitric acid: heated out of the contact of air, phosphate of lime and phosphuretted hydrogen gas are the results. This salt is useful for the preparation of other hypophosphites.

PHOSPHITE OF LIME is a difficultly-soluble salt, crystallizable by spontaneous evaporation. When its solution is heated, nacreous crystals of a *subphosphite* are deposited, and a very soluble and difficultly-crystallizable *biphosphite* remains dissolved.

PHOSPHATE OF LIME.—There appear to be several definite combinations of lime with phosphoric acid, among which the following have been particularly examined. (BERZELIUS, *Ann. de Ch. et Ph.*, ii. 167.)

1. NEUTRAL PHOSPHATE OF LIME. ($C + p'$).—When a solution of rhombic phosphate of soda is dropped into a solution of chloride of calcium, the latter being left in excess, a crystalline precipitate falls, which at a red heat loses water: it is white, tasteless, and consists of

Berzelius.					Berzelius.				
Lime	1	28	43·7	45·81	1	28	34·1	35·42
Phosphoric acid	1	36	56·3	54·19	1	36	43·9	41·90
Water	0	0	0·0	0·0	2	18	22·0	22·63
<hr/>					<hr/>				
Anhydrous	1	64	100·0	100·00	Crystallized	1	82	100·0	100·00

2. SUBPHOSPHATE OF LIME. BONE PHOSPHATE. ($\frac{1}{2}C + p'$).—This phosphate exists in bones and other parts of animals: it is formed when a solution of chloride of calcium is gradually dropped into the solution of rhombic phosphate of soda, the latter being left in excess; or whenever ammonia is added to any acid solution of phosphate of lime; or by adding neutral phosphate of ammonia to solution of chloride of calcium, in which case the fluid becomes acid. The tendency of phosphoric acid to form a basic or subsalt with lime is such, that if moist neutral phosphate of lime be mixed with a strong solution of chloride of calcium, hydrochloric acid is evolved on heating the mixture. This salt is white and insipid, and when recently precipitated, and boiled in water, a trace of it remains in solution, and if gelatine or starch be present a very sensible portion is taken up. Water, containing common salt or hydrochlorate of ammonia, also sparingly dissolves it. Dilute nitric, hydrochloric, and acetic acids dissolve it without decomposition, and ammonia throws it down unaltered. It is decomposed when digested in solution of sulphate of ammonia. Sulphuric acid converts it into sulphate and superphosphate of lime. At a very high temperature it fuses into a white opaque enamel. It is composed of

				Berzelius	Fuchs	Klaproth
				Artificial.	Artificial.	Apatite.
Lime	1½	42	53·8	51·68	54·74	53·75
Phosphoric acid	1	36	46·2	48·32	45·26	46·25
<hr/>				<hr/>		
Bone phosphate	1	78	100·0	100·00	100·00	100·00

Native Phosphate of Lime, identical in composition with the preceding, occurs crystallized and massive, and is known under the names of *apatite*, *asparagus-stone*, *moroxite*, and *phosphorite*. The crystallized variety is found in Cornwall and Devonshire, of singular beauty. Its primitive form is a six-sided prism: it also occurs in volcanic products; and, what is curious, the former is phosphorescent when heated, and the latter not. The massive variety is found in Bohemia and in Spain. The phosphorite which constitutes a rock exists in beds in Estremadura in Spain, and Schlackenwald in Bohemia; it is one of the most beautiful of the phosphorescent minerals, and when fragments of it are placed upon a hot iron they shine in the dark with a brilliant pale-green light.

3. SESQUIPHOSPHATE OF LIME ($C + \frac{1}{2}p'$) is obtained by adding alcohol to a saturated solution of the *neutral* phosphate in phosphoric acid; the precipitate, when washed with alcohol, consists of 1 propor-

tional of lime + $1\frac{1}{2}$ phosphoric acid. Water resolves it into an acid and an insoluble phosphate. (BERZELIUS, *Ann. de Ch. et Ph.*, ii. 173.)

4. BIPHOSPHATE OF LIME ($C + 2p'$) is formed, according to Berzelius, by digesting the *neutral* phosphate in phosphoric acid. On evaporation, crystalline scales are deposited, composed of 1 proportional of lime + 2 of phosphoric acid. The same salt is said to be obtained by digesting the neutral phosphate in hydrochloric or nitric acids, and evaporating the solution till it furnishes crystals. Distilled with charcoal, its excess of acid is decomposed and yields phosphorus, and a neutral phosphate remains.

5. SUPERPHOSPHATE OF LIME.—The phosphoric glass described under the head *Phosphorus* (p. 484), is considered by Dr. Thomson as a definite compound, which he has termed *quadruphosphate of lime*. (*System*, ii. 460.) If 100 parts of phosphate of lime be digested for twenty-four hours with 87 parts of sulphuric acid diluted with a sufficient quantity of water, and be then filtered, the liquor which passes through contains the whole of the phosphoric acid, with only one-fourth of the lime which existed in the original salt; the remaining three-fourths having formed an insoluble compound with the sulphuric acid. The dissolved salt, therefore, is a compound of 1 atom of lime = 28 + 4 atoms of acid = 112. When evaporated, it forms, on cooling, pearly scales, which have an acid taste, and dissolve readily in water, giving an acid solution of the specific gravity 1.44. When dried and fused in a crucible, a transparent glass is obtained, commonly called *glacial phosphoric acid*, and employed chiefly in the production of phosphorus. (HENRY, i. 567.) According to Berzelius, the decomposition of bone-earth by sulphuric acid is not attended by any definite result, but varies with the concentration and quantity of the acid, and is nearly complete when concentrated acid is added to a saturated solution of the superphosphate. Phosphate of lime is entirely decomposed when digested in a mixture of sulphuric acid and alcohol; sulphate of lime is precipitated, and an alcoholic solution of phosphoric acid, free from lime, is obtained. The solution of phosphate of lime in nitric acid, is decomposed by carbonate or acetate of lead; the lime remains in solution with the nitric acid, and the phosphoric acid is precipitated in combination with the oxide of lead.

SELENIURET OF CALCIUM.—The action of selenium upon lime has not been examined: when hydroselenic acid is passed into lime water the liquid is at first colourless, but it gradually reddens, even when out of the contact of air.

SELENITE OF LIME.—Berzelius has described a *neutral selenite* and a *biselenite of lime*. The former gradually falls in a pulverulent form, from a solution obtained by the action of selenious acid on carbonate of lime. If fused at a red heat in a glass vessel, it corrodes and passes through it. When dissolved in selenious acid small prismatic crystals of *biselenite of lime* are obtained, which are permanent in the air: when heated, or digested in ammonia, they lose acid, and become neutral. (*Ann. de Ch. et Ph.*, ix. 263.) The *seleniates* of lime have not been examined.

CARBONATE OF LIME, ($C + car'$), or $\text{Ca } \ddot{\text{C}}$, is the most abundant compound of this earth; it exists in all river and spring water, and, consequently, in the ocean, and is an essential ingredient in all fertile soils. When lime-water is exposed to air, it becomes gradually covered with an insoluble film of carbonate of lime: hence its use as a test of the presence of carbonic acid; but excess of carbonic acid redissolves it, producing a supercarbonate. Carbonate of lime is also precipitated by the carbonated alkalis from solutions of calcareous salts. It is a tasteless white powder, insoluble in pure water, and having no alkaline reaction. Exposed for a sufficient time to the joint action of a red heat and a current of air, the whole of the carbonic acid escapes, to the amount of 44 per cent., and quick-lime is obtained. Hence carbonate of lime consists of

				Kirwan.	Marcet.	Stromeyer.	Berzelius.
Lime	1	28	56	55	56.1	56.35	56.4
Carbonic acid .	1	22	44	45	43.9	43.65	43.6
Carbonate of lime	1	50	100	100	100.0	100.00	100.0

Mr. Daniell obtained crystals of carbonate of lime from a solution of lime in syrup. When a solution obtained by boiling together 1 part of hydrate of lime, 3 of sugar, and 6 of water, was filtered and exposed for fifteen days to the air, Gay Lussac found the whole of the lime deposited in acute rhombic crystals, consisting of 1 atom of carbonate of lime and 5 of water. In this case, the carbonic acid is derived from the atmosphere. These crystals are not changed by cold water, but in hot water, or exposed to air, they gradually fall to powder. Boiled in alcohol they retain their form, but lose 2 atoms of water, becoming ($C + car' + 3q$). (*Ann. de Ch. et Ph.*, xlviii. 301.)

Native Carbonate of Lime occurs in great abundance and in various forms. The primitive form of crystallized carbonate of lime, or *calcareous spar*, is an obtuse rhomboid of $105^{\circ} 5'$ and $74^{\circ} 55'$ (WOLLASTON), $101^{\circ} 50'$ and $78^{\circ} 50'$ (DUMAS). Its specific gravity is 2.72. It occurs in every kind of rock, and its secondary forms are more numerous than those of any other substance. Bournon, in his *Traité de Minéralogie*, has described and figured six hundred and eighty modifications. What is termed *Iceland spar* is this substance, in its primitive form, and of extreme purity: it is highly doubly refractive (p. 194) and transparent; some of the varieties are opaque or translucent, snow-white, or tinged of different hues. The mineral is recognised by its foliated and rhomboidal fracture, and its moderate hardness, being scratched by fluor-spar; before the blowpipe it loses carbonic acid, and becoming *lime*, is intensely luminous; it dissolves with effervescence in hydrochloric acid, and the solution, when much diluted, affords a white precipitate with oxalate of ammonia. Carbonate of lime sometimes forms *stalactites* and *stalagmites* (from *σταλαζω*, I drop, and *σταλαγμα*, a drop), of which some of the caverns of Derbyshire furnish magnificent specimens; it is there deposited from its solution in water acidulated by carbonic acid, and substances immersed in this water become incrustated by carbonate of lime when the excess of acid flies off, as seen in the *petrifying-well* at Matlock. A fibrous carbonate of lime, called *satin-spar*, is found in Cumberland.

A peculiar variety, originally found in Arragon in Spain, has been

termed *Arragonite*; it often occurs in six-sided crystals of a reddish colour, and harder than the common carbonate. There is an acicular or fibrous variety, found in France and Germany; and the white radiated substance, improperly called *flos ferri*, is also regarded as of the same species. Some varieties contain about 3 per cent. of strontia. The crystalline forms of Arragonite have been described in detail by Bournon (*Traité de Minéralogie*); the primary form is a right rhomboidal prism of $116^{\circ} 10'$ (BROOKE). They contain a little water, which they lose when heated, and crumble into powder; by which Arragonite is distinguished from calcareous spar. It is also heavier, its specific gravity being from 2.8 to 2.9.

All the varieties of *marble* and *limestone* consist essentially of carbonate of lime; of these, *white granular limestone*, or *primitive marble*, is most esteemed; there are, also, many coloured varieties of extreme beauty. It is distinguished from *secondary limestone* by the absence of organic remains, by its granularly foliated structure, and by its association with other primitive substances. The most celebrated statuary marble is that of Paros and Mons Pentelicus near Athens; of these, some of the finest specimens of ancient sculpture are composed. The marble of Carrara, or Luni, on the eastern coast of the Gulf of Genoa, is also much esteemed; it is milk-white and less crystalline than the Parian.

Many beautiful secondary marbles for ornamental purposes are quarried in Derbyshire, and especially the *black marble*, called also *Lucullite*, from the admiration bestowed on it by Lucius Lucullus. (PLINY, *Hist. Nat.*, 36, 8.) Its colour appears to depend upon a small quantity of carbonaceous matter. Westmoreland and Devonshire also afford beautiful varieties of ornamental marble; and in Anglesea, a marble intermixed with green serpentine is found, little inferior in beauty to the *verd antique*.

Among the inferior limestones, we enumerate many varieties, such as *common marble*; *bituminous limestone*, abundant upon the Avon, near Bristol, and known under the name of *swine-stone* or *stink-stone*, from the peculiar smell which it affords when rubbed; *Oolite* or *Roestone*, of which the houses of Bath are built; and its variety, called *Portland-stone*; *Pisolith* or *peastone* consisting of small rounded masses, composed of concentric layers, with a grain of sand in the centre; and lastly, *chalk* and *marl*.

All these substances are more or less useful for ornamental purposes, or for building; they afford *quicklime* when burned, and in that state are of great importance as *manures*, and as ingredients in the cements or *mortars* used for building. There is a great variety of limestones used for burning into quick-lime, and, generally speaking, any of the varieties may be employed which neither fuse nor crumble into powder at the temperature required to expel the carbonic acid, which is a full red-heat.

Lime-burning. Although all the species of limestone may, by burning, be brought to the state of quick-lime, the substances belonging to the family of *compact limestone* are the only ones that are employed for this purpose in the large way. Sometimes calcareous spar, and statuary marble, are used in the laboratory for the purpose of procuring a lime purer than ordinary. But owing to the crystalline texture of these substances, the laminae of which they are composed part from each other

during the volatilization of the carbonic acid, so that by the time they are rendered caustic, their cohesion is destroyed, and they are reduced to the state of sand, a circumstance which must always prevent them from being used in kilns of the common construction. The lime-kiln at present almost universally employed in this country, is a cup-shaped concavity, in a solid mass of masonry, open at top, and terminated at bottom by a grate, immediately above which is an iron door. This simple furnace is first charged with fuel, (either wood, or coal and cinders, but more commonly the latter,) upon which is afterwards laid a stratum about a foot thick of limestone, broken into pieces not larger than the fist; to this succeeds a charge of fuel: and so on alternately, keeping the kiln always full. The pieces of limestone descend towards the bottom of the kiln in proportion as the fuel is consumed, being in the mean time kept at a pretty full red-heat. At this temperature, the water and carbonic acid are driven off; and by the time the limestone arrives at the bottom of the kiln, which happens in about forty-eight hours, it is rendered perfectly caustic. The door above the grate is then opened, and the lime below the next descending stratum of fuel is raked out; the remaining contents of the furnace sink down, and a fresh charge is laid on the top. The compact limestone, after having undergone this process, though much lighter and more porous than before, still retains its figure unaltered: hence it is readily separable from the ashes of the fuel, and is sufficiently hard to be carried from place to place without falling to pieces. (AIKIN'S *Dictionary*, Art. LIME; URE'S *Dictionary of Arts*; and DUMAS, *Chimie app. aux Arts*, ii. 481.)

Attempts have been made to burn lime, or in other words, to expel the carbonic acid from limestone, in close vessels, but it is invariably found that the carbonic acid cannot, under such circumstances, be driven off; and, indeed, Bucholz found, that upon strongly heating five or six pounds of pure chalk, closely pressed into a crucible, and out of the access of air and its watery vapour, scarcely any carbonic acid was driven off; but, with the exception of a small portion upon the surface the contents of the crucible were converted into a hard, foliated, yellowish mass, retaining nearly the whole of the carbonic acid, semi-transparent, and evidently having undergone incipient fusion. (GEHLEN'S *Jour.*, Second Series, i. 271.) This agrees with Sir James Hall's experiments, who, by exposing powdered chalk to great heat and pressure, succeeded in fusing it (without escape of carbonic acid), and thus imitating the process of nature, by which he supposed *marble* to have been formed. (*Phil. Trans. Edinb.*, vol. vi.)

CYANURET OF CALCIUM has not been obtained. When hydrate of lime is digested in hydrocyanic acid, a solution of hydrocyanate of lime is formed, which upon evaporation is resolved into ammonia and carbonate of lime.

SULPHOCYANURET OF CALCIUM forms deliquescent acicular crystals, soluble in water and in alcohol.

BORATE OF LIME is a white tasteless powder of very difficult solubility in water. At a red heat it forms a vitreous mass.

FLUOBORATE OF LIME forms a gelatinous mass, which has an acid taste and reddens litmus. (BERZELIUS.)

CHARACTERS OF THE SALTS OF LIME.—These salts have the following properties: those which are *soluble* are not altered by pure ammonia, but they are decomposed by potassa and soda. They are also decomposed by the carbonates of potassa, soda, and ammonia, which produce precipitates of *carbonate of lime*. Oxalate of ammonia produces in their solutions a white insoluble precipitate of *oxalate of lime*, which, exposed to a red heat, affords carbonate of lime or pure lime. The soluble sulphates throw down sulphate of lime from such solutions of the salts of lime as are not very dilute. Such of the salts as are soluble in alcohol, tinge the edge of its flame of a reddish colour, much like the tint given by the salts of strontia. The *insoluble* salts of lime are decomposed by being boiled with carbonate of potassa, and afford *carbonate of lime*.

§ V. BARIUM.

THIS metal was discovered by Davy, in 1808; he obtained it by placing a globule of mercury upon moistened *baryta*, lying upon a plate of platinum, in connexion with the positive pole of a powerful Voltaic battery: the negative wire was then brought into contact with the mercury, which, combining with the evolved barium, gradually became an *amalgam*; this was heated out of the contact of air so as to distil off the mercury, and the barium remained. It may also be procured by passing potassium in vapour over baryta heated to redness in an iron tube, and afterwards withdrawing the reduced barium, which the residue contains, by means of mercury: the latter metal is separated by distillation in a retort, care being taken not to raise the temperature to redness, for then the barium decomposes glass. (GRAHAM.)

Barium has a specific gravity above 2. It is of a gray colour, and rapidly absorbs oxygen; when gently heated it burns with a red light; it decomposes water, evolving hydrogen, and forming a solution of baryta; its properties, however, have hitherto scarcely been ascertained. Its equivalent, deduced indirectly from its saturating power and from the action of chlorine on baryta, is 69. (68·6 GMELIN, 68·7 BERZELIUS and TURNER.)

OXIDE OF BARIUM. BARYTA, or BARYA ($ba + o$) or B, is obtained by exposing the crystals of pure *nitrate of baryta* for some time to a bright red-heat in a porcelain retort or covered crucible; it acts upon platinum, and if a silver crucible be employed the heat required for the perfect decomposition of the nitrate is such as to endanger its fusion. Baryta may also be obtained by subjecting artificial *carbonate of baryta* to an intense white heat thoroughly mixed with about 10 per cent. of finely powdered charcoal, in a plumbago crucible.

Graham uses *iodate of baryta*, a source of pure baryta: "it may be fused in a porcelain retort, and is more easily decomposed than the nitrate, and has not the troublesome property of fusing and swelling up when heated, which the latter salt possesses. The iodine comes off with the oxygen, and may be recovered."

Baryta is generally in the form of a porous mass, or gray powder, and

when pure, is very difficult of fusion. Its specific gravity is about 4, hence the name *Baryta*, as being the *heaviest* of the substances usually called *earths* (from *βαρυς*, *heavy*). It has a strong alkaline taste, and reaction on vegetable colours. It is insoluble in alcohol. It eagerly absorbs water, heat is evolved, and a white hydrate is formed. After long exposure to air it becomes white, and is a mixture of the hydrate and carbonate. *Baryta*, considered as a *protoxide of barium*, consists of

				Davy.	Berzelius.
Barium	1	69	89.6	89.7	89.55
Oxygen	1	8	10.4	10.3	10.45
Baryta	1	77	100.0	100.0	100.00

HYDRATE OF BARYTA. ($B + q$).—When pure baryta is sprinkled with water it absorbs it, becomes intensely hot, and even, according to Barry, incandescent, (*Ann. of Phil.*, Second Series, ii. 77,) and crumbles down into a bulky white powder, which fuses, but does not give out water at a red-heat. It is composed of

Baryta	1	77	89.5
Water	1	9	10.5
Hydrate of baryta	1	86	100.0

Hydrate of baryta dissolves in 20 parts of cold, and in 3 of boiling, water (DAVY), forming a solution which is a very delicate test of the presence of carbonic acid, and which speedily becomes covered with a film of carbonate of baryta when exposed to air. A saturated solution of baryta, in hot water, deposits flattened hexagonal prisms as it cools, containing, according to Dalton, 20, but according to Phillips, 10, equivalents of water. (*Phil. Mag.*, vi. 52, 3rd series.) According to Smith (*Phil. Mag.*, and *Annals*, vi. 53, and ix. 87), this hydrate contains 9 atoms of water, 7 of which it loses when dried upon a sand-bath, and retains 2; of these 1 is expelled at a red-heat, and 1 retained, forming the above protohydrate. *Baryta-water* is powerfully alkaline and poisonous.

PEROXIDE OF BARIUM. ($ba + 2 o$).—This compound is obtained when baryta is heated in oxygen, or when dry oxygen gas is passed over fragments of baryta, heated to dull-redness in a glass or porcelain tube: it may also be formed by adding 1 part of chlorate of potassa to 4 of baryta, previously heated to redness in a platinum crucible; the oxygen of the chlorate combines with the baryta, and, by the action of water, the remaining chloride of potassium may be washed out, and a *hydrated peroxide of barium* remains, composed of 1 equivalent of baryta, 2 of oxygen, and 6 of water. (WÖHLER and LIEBIG.) The application of this compound to the production of the *peroxide of hydrogen*, or *oxygenated water*, has already been pointed out (p. 393). When the anhydrous peroxide, which is of a gray colour, is put into water, it does not evolve heat, and becomes the white, pulverulent, and insoluble hydrate; when heated to 212° , it gives out an equivalent of oxygen, and reverts to the state of protoxide, which is soluble. When peroxide of barium is heated in hydrogen it becomes incandescent, emitting a greenish flame and absorbing the gas; protohydrate of baryta is the product.

CHLORIDE OF BARIUM. (*ba + c.*)—This compound may be obtained by heating baryta in chlorine, in which case oxygen is evolved; or in hydrochloric acid gas, when it becomes red-hot, and chloride of barium and water are the results. It is generally formed by dissolving carbonate of baryta in diluted hydrochloric acid, evaporating to dryness, and fusing the residue in a covered platinum crucible. It may also be produced by exposing a mixture of equal parts of powdered sulphate of baryta and chloride of calcium to a red-heat for an hour, in a covered Hessian crucible; the salts fuse and mutually decompose each other: when the crucible has cooled, its contents are powdered, put into boiling water, well stirred together, and filtered as rapidly as possible, otherwise sulphate of baryta would be recomposed; on evaporating the filtered liquid crystals of chloride of barium are obtained, whilst the undecomposed chloride of calcium remains in solution. (DUMAS.)

Chloride of barium, after it has been fused at a red-heat, is of a grayish colour; its taste is acrid, it is not deliquescent, it is insoluble in absolute alcohol, (said to be soluble in 400 parts of anhydrous alcohol; GRAHAM.) It is generally kept in aqueous solution commonly known under the name of *muriate of baryta*, and is in constant use in the laboratory as a test and precipitant for sulphuric acid: this, by evaporation, yields flat four-sided crystals, bevelled at their edges, and permanent in ordinary states of the atmosphere, but efflorescent, from the loss of water of crystallization, in a very dry air at 60° . At 212° the water is soon expelled, and anhydrous chloride remains. 100 parts of water at 60° dissolve about 43 parts of these crystals, and at 222° , which is the boiling-point of the saturated solution, 100 of water dissolve 78. The anhydrous chloride of barium consists of

Barium	. . .	1	. . .	69	. . .	65.7
Chlorine	. . .	1	. . .	36	. . .	34.3
Chloride of barium		1		105		100.0

The crystals contain, according to Phillips, 14.5 *per cent.* of water (*Ann. of Phil.*, N. S., vi. 342). As sold by chemists, their solution often gives a precipitate with pure ammonia owing to the presence of chloride of lead. (A. TAYLOR.) The composition of the crystals is

Chloride of barium	1	. . .	105	. . .	85.4
Water	2	. . .	18	. . .	14.6
Crystals of hydrated chloride of barium		1		123		100.0

CHLORATE OF BARYTA (*B + C'*) was formed by Chenevix in the same way as chlorate of potassa, namely, by passing chlorine through an aqueous solution of baryta; but, in consequence of the similar solubility of chloride of barium and chlorate of baryta, considerable difficulty attended the separation of the products. It was effected by adding to the solution of the mixed salts, a solution of phosphate of silver in acetic acid, by which the chloride of barium was decomposed and resolved into chloride of silver and phosphate of baryta, both of which are insoluble. Chlorate of baryta may also be obtained by saturating chloric acid (obtained by the action of chlorine upon oxide of silver diffused in water) with hydrate of baryta: or it may be formed, as suggested by Mr.

Wheeler, by adding a hot solution of chlorate of potassa to a solution of silicated hydrofluoric acid; the potassa is precipitated in the form of an insoluble silico-fluoride of potassium, and the chloric acid remains in solution, and may be saturated with carbonate of baryta, which throws down any excess of the silicated fluoric acid, and leaves chlorate of baryta in solution, from which the salt may be obtained by evaporation.

Chlorate of baryta forms square prismatic crystals, soluble in about 4 parts of water at 60° , and insoluble in alcohol; they contain 1 equivalent of water. Sprinkled with sulphuric acid they become luminous. By heat they are resolved into oxygen and chloride of barium. They are decomposed by dilute sulphuric acid, furnishing sulphate of baryta and chloric acid, and are the readiest source of that acid (p. 370). The anhydrous salt consists of

Baryta	1	77	50.3	47.3
Chloric acid . .	1	76	49.7	52.7
Chlorate of baryta	1	153	100.0	100.0

Chenevix.

IODIDE OF BARIUM ($ba+i$) is formed by acting upon baryta, or carbonate of baryta, by hydriodic acid, evaporating the solution, and heating the residue. It may also be formed by passing hydriodic acid gas over baryta; the action is very intense, and it is stated by Dumas, that even when the gas is cooled down to 0° the baryta becomes incandescent: the baryta and the acid are of course mutually decomposed, and water and iodide of barium are the products.

Iodide of barium may be obtained in acicular crystals; it is very soluble in water, somewhat deliquescent, and when exposed to the air carbonate of baryta is formed and a portion of iodine set free. It is not fusible at a red heat, and if a current of oxygen be then directed upon it the vapour of iodine appears and it becomes alkaline, whence it may be inferred that the affinity of barium for oxygen is greater than for iodine. (DUMAS.) It consists of

Barium	1	69	35.4
Iodine	1	126	64.6
Iodide of barium	1	195	100.0

IODATE OF BARYTA. ($B+i'$).—When iodine is added to baryta-water, iodide of barium and iodate of baryta are the results; the latter salt, in consequence of its little solubility, falls in the form of a white precipitate, which may be purified by washing it upon the filter. It is also formed by double decomposition when iodate of potassa is added to a soluble barytic salt. At 62° it requires about 300 parts of water for its solution. Exposed to heat it gives out oxygen and iodine, and baryta remains. (GAY LUSSAC, *Ann. de Ch. et Ph.*, xci. 81.) It consists of

Baryta	1	77	31.7
Iodic acid . . .	1	166	68.3
Iodate of baryta	1	243	100.0

BROMIDE OF BARIUM ($ba+b$) is obtained by adding baryta to the ethereal solution of bromine; or by saturating hydrobromic acid with

baryta and evaporating to dryness; or by boiling excess of protobromide of iron with freshly-precipitated carbonate of baryta, filtering, and evaporating to dryness; it is fusible, soluble in water and in alcohol, and crystallizes in opaque mammellated masses; or, according to M. Henry, Jun., in white rhombic prisms, of a bitter taste, and consisting of

Barium	. . .	1	. . .	69	. . .	46.9
Bromine	. . .	1	. . .	78	. . .	53.1
<hr/>						
Bromide of barium	1			147		100.0

BROMATE OF BARYTA ($B+b'$) has already been mentioned as a source of bromic acid (p. 377): it forms acicular crystals, slightly soluble in cold water, and producing vivid combustion and a green flame on hot charcoal. It is obtained along with the bromide, by the action of bromine on solution of baryta. (BALARD, *Ann. de Ch. et Ph.*, xxxii. 367.)

Its composition is

Baryta	. . .	1	. . .	77	. . .	39.5
Bromic acid	. . .	1	. . .	118	. . .	60.5
<hr/>						
Bromate of baryta	1			195		100.0

FLUORIDE OF BARIUM ($ba+f$) is best obtained, according to Berzelius, by adding fresh precipitated and moist carbonate of baryta to hydrofluoric acid; carbonic acid is expelled, and the fluoride remains in the form of a white powder, very sparingly soluble in water, but soluble in hydrochloric and nitric acids. It forms a double salt with chloride of barium.

NITRATE OF BARYTA ($B+n'$) may be produced by dissolving the native carbonate in nitric acid, evaporating to dryness, redissolving and crystallizing; or by decomposing a solution of sulphuret of barium by dilute nitric acid. It forms permanent octoëdral and cubo-octoëdral crystals, which are anhydrous: their forms have been described by Brooke (*Ann. of Phil.*, N. S., vii. 21). The taste of this salt is acrid and astringent. It is soluble in 12 parts of cold and 4 of boiling water; or, according to Gay Lussac, 100 parts of water, at 32° , dissolve 5 parts; at 58° , 15.8 parts; at 120° , 17 parts; and at 215° , 35.2 parts. It is insoluble in alcohol. It is decomposed with decrepitation by a bright-red heat, furnishing pure baryta: this decomposition should be effected in a porcelain crucible; for if platinum be used it is acted upon, and the baryta contaminated by oxide of platinum.

If a moderately-strong solution of the nitrate of baryta be added to nitric acid, a precipitation of nitrate of baryta takes place, in consequence of the insolubility of the nitrate in the acid; hence, in using nitrate of baryta as a test of the presence of sulphuric acid in nitric acid, the latter should be considerably diluted previous to its application. Nitrate of baryta is composed of

				Berzelius.	Kirwan.	
Baryta	. . .	1	. . . 77	. . . 58.7	. . . 58.8	. . . 57
Nitric acid	. . .	1	. . . 54	. . . 41.3	. . . 41.2	. . . 43
<hr/>						
Nitrate of baryta	1		131	100.0	100.0	100

When nitrate of baryta is heated till nitrous acid is no longer evolved, a compound of baryta and nitric oxide remains, which may be obtained from its aqueous solution in crystals, constituted of—

			H. Hess.
Baryta . . .	1 . .	77 . .	61·5
Nitric oxide . .	1 . .	30 . .	24·0
Water . . .	2 . .	18 . .	14·5
	<u>1</u>	<u>125</u>	<u>100·0</u>

SULPHURET OF BARIUM ($ba + s$) is formed by passing sulphuretted hydrogen over red-hot baryta in a glass tube; or by fusing a mixture of sulphur and baryta in a retort. It may also be obtained by the action of hydrogen or charcoal upon ignited sulphate of baryta. The easiest process is to mix sulphate of baryta, in fine powder, into a paste with an equal volume of flour, place it in a Hessian crucible, on which a cover is luted, and expose it to a white-heat for an hour or two, raising the temperature slowly. On pouring hot water on the ignited mass the sulphuret of barium is dissolved, and may be separated from undecomposed sulphate and excess of charcoal by filtration. (TURNER.) It is readily soluble in hot water, and the solution, on cooling, deposits hydrated crystals. By exposure to air, the solution absorbs carbonic acid and oxygen, yielding carbonate and hyposulphite of baryta. It dissolves sulphur, but in what proportions has not been ascertained. When its solution is boiled with peroxide of copper till it ceases to blacken acetate of lead, and filtered whilst hot, it yields on evaporation pure baryta; mixed with carbonate of potassa it yields carbonate of baryta; with hydrochloric acid, chloride of barium; and with dilute nitric acid, nitrate of baryta. It consists of

Barium	1 . .	69 . .	81·2
Sulphur	1 . .	16 . .	18·8
Sulphuret of barium	1	85	100·0

HYPOSULPHITE OF BARYTA. ($B + \bar{S}$).—This salt is thrown down on pouring a solution of chloride of barium into a solution, not too dilute, of hyposulphite of lime: it is a white powder, soluble without decomposition in hydrochloric acid; at a low heat it takes fire, and sulphur burns off. When the solutions from which it is precipitated are dilute, it falls after some minutes, in small crystalline grains, followed by a copious separation of the salt. According to Herschel (*Edin. Phil. Jour.*, i. 20), this salt consists of

Baryta	1 . .	77 . .	61·6
Hyposulphurous acid . .	1 . .	48 . .	38·4
Hyposulphite of baryta	1	125	100·0

SULPHITE OF BARYTA ($B + \bar{S}$) is insoluble in water, and formed by adding sulphite of potassa to a solution of chloride of barium. It dissolves in sulphurous acid, and the solution furnishes acicular and tetraëdral crystals when very slowly evaporated. It passes into sulphate by long exposure to air: at a red heat it gives out sulphur and becomes sulphate. It consists of

Baryta	1 . .	77 . .	70·6
Sulphurous acid . . .	1 . .	32 . .	29·4
Sulphite of baryta	1	109	100·0

HYPOSULPHATE OF BARYTA. ($B + S'$).—When sulphurous acid gas is passed into water holding finely-powdered peroxide of manganese in suspension, a neutral solution is obtained, composed of sulphate and hyposulphate of manganese. These salts are decomposed by excess of baryta, and a soluble *hyposulphate of baryta* is formed, through which carbonic acid is passed, in order to saturate any excess of baryta; and the whole being heated to drive off carbonic acid, which holds a little of the carbonate in solution, the hyposulphate of baryta is obtained, and may be purified by crystallization. The solution of this salt may be decomposed by the careful addition of sulphuric acid, and the *hyposulphuric acid* is thus obtained in solution, as already stated (p. 475).

The hyposulphate of baryta crystallizes in quadrangular prisms, variously terminated. It dissolves, according to Gay Lussac, in 1.1 times its weight of water at 212° ; in 4 times its weight at 64° . It is insoluble in alcohol. At a red-heat it gives out water and sulphurous acid, and leaves seven-tenths its weight of neutral sulphate of baryta. The crystallized salt consists of

				Welter and Gay Lussac.	Heeren.
Baryta	1	77	46.1	46.03	45.93
Hypsulphuric acid	1	72	43.1	43.41	43.31
Water	2	18	10.8	10.56	10.76
	1	167	100.0	100.00	100.00

When a solution of this bihydrated salt is set aside to evaporate spontaneously, large four-sided prismatic crystals, terminated by four-sided pyramids, are gradually deposited, which, according to Heeren, are a *quater-hydrated hyposulphate of baryta* ($B + S' + 4Q$), composed therefore of

				Heeren.
Baryta	1	77	41.6	41.88
Hypsulphuric acid	1	72	38.9	39.49
Water	4	36	19.5	18.63
	1	185	100.0	100.00

SULPHATE OF BARYTA ($B + S'$) is an abundant natural product; it is insoluble in hot and cold water, and therefore precipitates whenever sulphuric acid, or a soluble sulphate, is added to any soluble salt of baryta; hence the solutions of baryta are accurate tests of the presence of sulphuric acid, and are also used in analysis to determine its quantity. If sulphuric acid be poured upon caustic baryta, the heat is so intense as to cause ignition. If the acid be boiled upon the finely-powdered or recently-precipitated sulphate, a portion is taken up; the whole of which, however, falls again upon diluting the solution with water. The extreme insolubility of this sulphate renders the soluble salts of baryta such delicate tests of the presence of sulphuric acid, that a millionth part in solution may, according to Pfaff, be detected by a slight white cloud. When the sulphuric acid is in combination the test is somewhat less delicate, but it shows the presence of 1 part of sulphate of soda in 400,000 of water. Recently-precipitated sulphate of baryta is sometimes very obstinate in subsiding from water, and will not only long remain suspended, but adheres to the glass, and will even pass through filtering-

paper: heat, and a little excess of acid, generally facilitates its deposition. It may be safely heated to redness without risk of change, and hence the filter containing it, in some cases of quantitative analysis, may be conveniently burned away.

Sulphate of baryta is an anhydrous compound of

				Klaproth.	Berzelius.
Baryta	1	77	65.8	66.7	65.643
Sulphuric acid . .	1	40	34.2	33.3	34.357
Sulphate of baryta	1	117	100.0	100.0	100.000

Native Sulphate of Baryta, Heavy Spar, or Baroselenite, is principally found in the mines of Westmoreland and Cumberland, and in Transylvania, Hungary, Saxony, and Hanover. A variety met with in Derbyshire, is called *cawk*. It occurs massive, stalactitic, and crystallized in a great variety of forms. Its primitive figure is a rhomboidal prism, the angles of which are $101^{\circ} 42'$, and $78^{\circ} 18'$. It is harder than carbonate of lime, but not so hard as fluor-spar. Its specific gravity is 4.7.

When native sulphate of baryta is heated it decrepitates, and at a very high temperature fuses into an opaque white enamel: it was employed in the manufacture of *jasper-ware* by the late Mr. Wedgwood, and for the production of opaque white patterns and figures, upon a coloured ground. When formed into a thin cake with paste, and heated to redness, it acquires the property of phosphorescence, as was first ascertained by Vincenzo Cascariolo, of Bologna, whence the term *Bologna phosphorus* was applied to it (p. 215). The artificial sulphate of baryta is used as a pigment, under the name of *permanent white*; it is very useful for marking phials and jars in a laboratory, not being discoloured by sulphuretted hydrogen, as is the case with white lead.

Decomposition of Sulphate of Baryta.—As the native sulphate is a common and abundant compound, several processes have been contrived for obtaining from it pure baryta. This may be effected by reducing the crystallized sulphate to a fine powder, and heating it red-hot for half an hour in a silver crucible with three parts of carbonate of potassa: the fused mass is then boiled repeatedly in water, till it no longer affords anything soluble in that liquid; the insoluble residue, consisting chiefly of carbonate of baryta, may be digested in dilute nitric acid, by which nitrate of baryta is formed, and which will yield the pure earth by exposure to heat as above mentioned. Another method consists in exposing to a red-heat, in an earthen crucible, a mixture of 6 parts of finely-powdered sulphate of baryta with 1 of powdered charcoal, for half an hour. This converts the sulphate into sulphuret, which is to be dissolved in hot water, the solution filtered and mixed with solution of carbonate of soda as long as it occasions a precipitate, which, when washed and dried, is carbonate of baryta. Or, by adding hydrochloric acid to the liquid sulphuret, sulphur is thrown down, and sulphuretted hydrogen evolved, and chloride of barium formed, which may be filtered off, and if required, decomposed by carbonate of potassa. Or the sulphuret, as it comes out of the crucible, may be thrown into *dilute* nitric acid, by which sulphuretted hydrogen is evolved, and nitrate of baryta formed, from the solution of which crystals are easily obtained by evaporation. Another method of decomposing a solution of sulphuret of barium consists in

adding to it oxide of copper till it ceases to blacken acetate of lead; it may then be quickly filtered, and a solution of baryta is obtained. (MOHR.) In this process 6 equivalents of sulphuret of barium and 8 of oxide of copper produce 5 of baryta, 1 of hyposulphite of baryta, and 4 of subsulphuret of copper. Peroxide of manganese may be substituted for oxide of copper, but it generally gives a solution of baryta coloured by some impurity. (GRAHAM.) When sulphate of baryta, in very fine powder, is boiled in a solution of carbonate of potassa or soda, a portion of the sulphate is also decomposed, and an equivalent proportion of carbonate of baryta formed: this decomposition of the sulphate is, however, never entire.

PHOSPHURET OF BARIUM is produced by passing phosphorus over heated baryta; there is an intense action, and phosphate of baryta, together with a phosphuret of a metallic lustre, is obtained, which acts upon water, evolving phosphuretted hydrogen, and affords a solution containing hypophosphite of baryta.

HYPOPHOSPHITE OF BARYTA ($B + \bar{p}$) may be obtained by the same process as hypophosphite of lime, namely, by boiling phosphorus with baryta in water; like the other hypophosphites it is very soluble in water, and difficultly crystallizable. (DULONG, *Ann. de Ch. et Ph.*, ii. 142.)

PHOSPHITE OF BARYTA ($B + \bar{p}$) was obtained by Berzelius, by adding a solution of chloride of barium to phosphite of ammonia; a crystalline crust of phosphite of baryta was formed in 24 hours. (*Ann. de Ch. et Ph.*, ii. 231.) A red-heat converts it into neutral phosphate of baryta with the evolution of hydrogen. It dissolves in phosphorous acid, forming, apparently, a distinct *biphosphite of baryta*. It consists of

				Berzelius.
Baryta	1	77	67.5	67.24
Phosphorous acid	1	28	24.5	24.31
Water	1	9	8.0	8.45
Crystallized phosphite of baryta	1	114	100.0	100.00

PHOSPHATE OF BARYTA. ($B + p'$).—When a solution of neutral phosphate of ammonia is dropped (not in excess) into a neutral barytic solution, an insoluble white powder falls, which melts into a gray enamel when strongly heated, and is soluble in hydrochloric, nitric, and phosphoric acid. It consists of

				Berzelius.
Baryta	1	77	68.1	68.2
Phosphoric acid	1	36	31.9	31.8
Phosphate of baryta	1	113	100.0	100.0

SESQUIPHOSPHATE OF BARYTA.—When a saturated solution of phosphate of baryta in phosphoric acid is mixed with alcohol, a bulky precipitate falls, which, when dried, forms a light, white, tasteless, powder; composed of

				Berzelius.
Baryta	1	77	58.8	60.87
Phosphoric acid	$1\frac{1}{2}$	54	41.2	39.13
Sesquiphosphate of baryta	1	131	100.0	100.00

BIPHOSPHATE OF BARYTA.—Biphosphate of soda occasions no precipitate in solution of chloride of barium. When a saturated solution of neutral phosphate of baryta in phosphoric acid is carefully evaporated, it yields crystals, which, after having been dried on filtering-paper, are permanent in the air. Water resolves them into phosphoric acid and neutral phosphate. (BERZELIUS, *Ann. de Ch. et Ph.*, ii. and xi.) At a red heat they lose water of crystallization, and a white spongy mass is formed. The crystals of this salt contain 2 proportionals of water; in its anhydrous state, it consists of

Baryta	1	77	51.7	Berzelius, 52.2
Phosphoric acid	2	72	48.3	47.8
Biphosphate of baryta	1	149	100.0	100.0

Berzelius found, on digesting neutral phosphate of baryta in ammonia, that a portion of the acid was abstracted, leaving a definite combination of 5 proportionals of baryta with 1 of acid.

SELENITE OF BARYTA falls in the form of a white insoluble powder, when solution of selenite of potassa is added to chloride of barium. *Biselenite of baryta* is formed by dissolving carbonate of baryta in selenious acid; it forms a granular crystalline powder very difficultly soluble in water.

SELENIATE OF BARYTA resembles the sulphate in insolubility.

CARBONATE OF BARYTA. (B + *car'*).—This salt falls in the form of a white powder, when the soluble salts of baryta are precipitated by the alkaline carbonates. For this purpose carbonate of ammonia is preferable to the carbonates of soda or potassa, for portions of the fixed alkalis are apt to go down with the baryta. Other methods of obtaining carbonate of baryta are stated under the head *Sulphate of Baryta*. It is so nearly insoluble, that water at 60° only takes up about 1-4300th, and at 212° about 1-2300th part. Water saturated with carbonic acid dissolves 1-820th. It has no action on vegetable colours: it is highly poisonous. When *baryta-water* is added to solutions of the carbonated alkalis, it abstracts their carbonic acid. Like the other carbonates, it is decomposed by the stronger acids with effervescence. It consists of

Baryta	1	77	77.8	Withering. 78.6	Berzelius. 77.9
Carbonic acid	1	22	22.2	21.4	22.1
Carbonate of baryta	1	99	100.0	100.0	100.0

Native Carbonate of Baryta was first discovered at Anglesark, in Lancashire, by Dr. Withering, and hence acquired the name of *Witherite*. It has also been found in Wales, Cumberland, Durham, Westmoreland, and Shropshire. Its primitive crystal is an obtuse rhomboid: sometimes it forms pyramidal six-sided prisms. That found in Lancashire is in globular masses of a radiated structure. Its density is 4.33. It is useful as a source of pure baryta and its salts. Though scarcely soluble in water, it is poisonous, probably in consequence of its solubility in the acids of the stomach. It dissolves more sparingly in solution of carbonic acid than the precipitated carbonate, and is more difficultly decomposed; but

if mixed with charcoal-powder, and kept for some time at a high red-heat, carbonic oxide escapes, and pure baryta is formed.

CYANURET OF BARIUM (*ba + cy*) is precipitated in the form of a white powder when hydrocyanic acid is mixed with baryta-water. It is also formed by heating ferrocyanuret of barium in a retort, for it is not decomposed at a temperature which destroys the cyanuret of iron: it is sparingly soluble in water, and the solution soon becomes covered by a film of carbonate of baryta, when in contact with air.

CYANATE OF BARYTA. (*B + cy*).—When cyanogen is passed through a mixture of hydrate of baryta and water, cyanate of baryta and cyanuret of barium are formed: the latter may be decomposed by a stream of carbonic acid: the filtered liquor then yields, when concentrated by evaporation and mixed with alcohol, small prismatic crystals; when their aqueous solution is evaporated, it decomposes into carbonate of baryta and ammonia.

SULPHOCYANURET OF BARIUM is formed by heating ferrocyanuret of barium with sulphur: it is soluble in water, and forms brilliant acicular crystals, which are slightly deliquescent.

BORATE OF BARYTA is formed by mixing a soluble salt of baryta with a solution of borax, and fusing the washed precipitate: it is a gray transparent glass, very sparingly soluble in water; before fusion it is a *hydrated salt*, somewhat more soluble in water, and its solution, according to Berzelius, is decomposed by carbonic acid. It is composed of

				Thenard.	Berzelius.	L. Gmelin.
Baryta 1	77 53	57.8 55.8	54.9			
Boracic acid . . 1	68 47	42.2 44.2	45.1			
Borate of baryta 1	145	100	100.0	100.0	100.0	100.0

BOROFLUORIDE OF BARIUM.—Carbonate of baryta is added to the aqueous solution of fluoboracic acid, as long as it is dissolved: on evaporation some boracic acid first separates, and afterwards prismatic crystals of the borofluoride, soluble in water without decomposition, and deliquescent in damp air: they contain 10.34 *per cent.* of water: they are decomposed at a red-heat; liquid fluoboric acid first passes off, then fluoboric gas; and fluoride of barium remains.

PROPERTIES OF BARYTIC SALTS.—The soluble barytic salts furnish white precipitates of carbonate and sulphate of baryta, upon the addition of carbonate or sulphate of soda. They give a yellow tinge to the flame of spirit of wine. The sulphate is insoluble in nitric acid and in the alkalis, and very sparingly soluble in sulphuric acid. A saturated aqueous solution of sulphate of strontia is a good test for the salts of baryta; it requires to be used in pretty large quantity, and the solutions to be tested should be neutral or nearly so. (A. TAYLOR.) Nearly all the barytic compounds are poisonous; sulphate of baryta is, however, harmless: the safest antidote, therefore, is solution of sulphate of soda. (ORFILA, *Traité de Poisons*; CHRISTISON *on Poisons*.) Chloride of barium has been employed in medicine, but the principal use of baryta is in the chemical laboratory. It is possible that pure baryta might be economically used for the decomposition of sulphate of soda, to obtain the pure alkali.

§ VI. STRONTIUM.

Strontia (or *strontites*) was first discovered in the state of *carbonate* at Strontian in Argyleshire, and was supposed to be a carbonate of baryta. Crawford, in 1790, pointed out some of its distinctive characters, but it was first shown to contain a peculiar earth by Dr. Hope, in 1792, (*Edin. Phil. Trans.*, iv.,) and by Klaproth in 1793, (*CRELL's Annals*, 1793 and 1794.) It is a substance of rare occurrence. The existence of *strontium*, as the metallic base of the earth *strontia*, was first demonstrated by Davy in 1808. It is probably as heavy as barium, and resembles it in appearance and in its leading chemical characters; it has, however, been as yet very imperfectly examined. The equivalent of strontium deduced from the best analyses of its compounds is 44, (43·8 TURNER, 43·85 GRAHAM, 44 GMELIN.)

PROTOXIDE OF STRONTIUM. STRONTIA. (*str* + *o*) or STR.—Strontium is rapidly oxidized by exposure to air, and it decomposes water, evolving hydrogen, and forming the oxide. Strontia may be obtained from the nitrate, the carbonate, and the sulphate of strontia, by processes similar to those directed in regard to baryta. It is a grayish-white substance; its specific gravity is between 3 and 4; it is extremely infusible, not volatile, has an acrid taste, and an alkaline reaction upon vegetable colours. It consists of

				Stromeyer.	Davy.	Berzelius.
Strontium	. 1 . .	44 . .	84·6 .	84·67 . .	86 . .	84·55
Oxygen	. 1 . .	8 . .	15·4 .	15·33 . .	14 . .	15·45
Strontia	1	52	100·0	100·00	100	100·00

HYDRATE OF STRONTIA. (*Str* + *q*.)—When strontia is sprinkled with water it heats and falls to powder like baryta, forming a solid hydrated compound of 1 equivalent of strontia=52, and 1 of water=9; it fuses, but does not part with its water, at a red heat. It is insoluble in alcohol. It dissolves in about 160 parts of water at 60°, forming *strontia-water*. Boiling water dissolves it more abundantly, and on cooling deposits crystals in the form of thin quadrangular tables: their primary form is a right square prism (BROOKE, *Ann. of Phil.*, 2nd series, vii. 287); they are soluble in 50 parts of cold and 2 of boiling water (DALTON), and are converted by heat into the protohydrate. They contain according to Phillips (*Phil. Mag.*, 3rd series, vi. 52) 63·76 *per cent.* of water, and consist, therefore, of 1 equivalent of strontia=52, and 10 equivalents of water=90.

PEROXIDE OF STRONTIUM may probably be formed by passing oxygen over strontia at a proper temperature, but it has not, I believe, hitherto been so obtained. When peroxide of hydrogen is mixed with strontia-water, brilliant crystalline scales are thrown down, composed according to Thenard of 1 equivalent of strontium and 2 of oxygen. (*str* + 2 *o*.) Dumas says that strontia does not absorb oxygen when it is heated in that gas, and that the precipitate thrown down by oxygenated water is a hydrated binoxide of strontium.

CHLORIDE OF STRONTIUM. (*str* + *c.*)—When strontia is heated in chlorine, it evolves 1 volume of oxygen for every 2 volumes of chlorine that are absorbed, and a chloride of strontium is the result. Heated in hydrochloric acid, strontia absorbs the gas with ignition and evolution of water. Chloride of strontium is generally obtained by dissolving *carbonate of strontia* in diluted hydrochloric acid, evaporating to dryness, and fusing the residue. It is of a gray colour and an acrid taste. It dissolves in alcohol, and the solution burns with a purplish-red flame. Its aqueous solution furnishes, upon evaporation, hexagonal prismatic crystals, which are deliquescent and soluble in 2 parts of water at 60°. They contain 40·5 *per cent.* of water of crystallization. (BERZELIUS.) 100 parts of anhydrous chloride of strontium rapidly absorb 84·5 of dry ammonia, falling into a light bulky powder, which loses ammonia when heated. (H. ROSE, *Ann. de Ch. et Ph.*, Lxii. 316.) The anhydrous or fused chloride consists of

Strontium.	1	44	55	Davy. 58
Chlorine	1	36	45	42
Chloride of strontium	1	80	100	100

CHLORATE OF STRONTIA (*STR* + *c'*) is obtained in the same way as the chlorate of baryta; it is a very soluble and deliquescent salt, difficultly crystallizable, and detonates when thrown upon red-hot coals with a beautiful purple light. It dissolves in alcohol.

IODIDE OF STRONTIUM (*str* + *i*) may be formed as iodide of barium. Dissolved in water, and carefully evaporated, it furnishes delicate prismatic crystals (*Hydriodate of Strontia*), which, heated in close vessels, fuse without decomposition; heated in the open air, iodine escapes, and strontia is generated. Iodide of strontium consists of

Strontium	1	44	26
Iodine	1	126	74
Iodide of strontium	1	170	100

IODATE OF STRONTIA (*STR* + *i'*) is obtained as iodate of baryta: it is soluble in 4 parts of cold water, and is resolved at a red heat into oxygen, iodine, and strontia.

BROMIDE OF STRONTIUM and **BROMATE OF STRONTIA** have not been examined.

FLUORIDE OF STRONTIUM is a very difficultly soluble white powder, obtained in the same way as fluoride of barium.

NITRATE OF STRONTIA. (*STR* + *n'*).—This salt is obtained by processes similar to those for obtaining *nitrate of baryta*: it crystallizes in octoëdrons: it is soluble in 5 parts of water at 60°, and in half its weight of boiling water. It is insoluble in anhydrous alcohol. Its taste is pungent and cooling. At a red heat the acid is evolved and decomposed, and strontia remains. According to Stromeier, the crystallized salt, as ordinarily prepared, contains no water of crystallization. It is used in the *red fire* employed at the theatres, which consists of 40 parts of dry

nitrate of strontia, 13 of powdered sulphur, 5 of chlorate of potassa, and 4 of sulphuret of antimony. The chlorate and sulphuret should be separately powdered, and mixed together on paper with the other ingredients; a very small quantity of powdered charcoal may also be added. When nitrate of strontia is finely powdered and mixed with spirit of wine, it communicates a beautiful red tint to its flame. It is composed of

				Stromeyer.	Cooper.	Richter.
Strontia	1	52	49	49.38	49.08	48.6
Nitric acid	1	54	51	50.62	50.92	51.4
Nitrate of strontia	1	106	100	100.00	100.00	100.0

When a moderately-strong solution of the above *anhydrous nitrate* is set aside, it sometimes deposits at a low temperature *oblique rhombic crystals*, (BROOKE, *Ann. of Phil.*, 2nd series, vii. 288,) composed of

Strontia	1	52	36.6
Nitric acid	1	54	38.0
Water	4	36	25.4
Hydrated nitrate of strontia	1	142	100.0

SULPHURET OF STRONTIUM (*Str* + *S*) may be formed by fusing strontia and sulphur in a green-glass tube; or by exposing the powdered sulphate to a high red-heat with charcoal. It dissolves in water with the same phenomena as sulphuret of barium, and its solution furnishes, by cautious evaporation, crystals of *hydrosulphuret of strontia*. When strontia or sulphuret of strontium is dissolved in water by a current of sulphuretted hydrogen, and the solution evaporated in vacuo, square prismatic crystals are obtained, which, when heated, fuse and give off water and sulphuretted hydrogen, sulphuret of strontium remaining in the form of a white powder. (BERZELIUS.)

HYOSULPHITE OF STRONTIA (*Str* + *S*^h) is formed by passing sulphurous acid into the solution of the sulphuret, or by exposing it to air: it crystallizes in rhomboids permanent at common temperatures, and soluble in about 5 parts of water at 60°. (GAY LUSSAC, *Ann. de Chim.*, LXXXV.) According to Herschel, this salt is doubly refractive. Its taste is bitter, and it is insoluble in alcohol. The crystals consist of

			Gay Lussac.
Strontia	1	52	35.9
Hyosulphurous acid	1	48	33.1
Water	5	45	31.0
Crystallized hyosulphite of strontia	1	145	100.0

SULPHITE OF STRONTIA (*Str* + *S*^h) is tasteless, nearly insoluble, and becomes *sulphate* by exposure to air.

HYOSULPHATE OF STRONTIA (*Str* + *S*^h) crystallizes in hexangular tables, soluble in 4.5 water at 60°, and in 1.5 at 212°; insoluble in alcohol; bitter, permanent, and leaving 0.577 of *sulphate* of strontia after heating to redness. They consist of—

Strontia	1	52	32.5	Heeren. 32.54
Hyposulphuric acid	1	72	45.0	45.36
Water	4	36	22.5	22.10
Crystallized hyposulphate of strontia	1	160	100.0	100.00

SULPHATE OF STRONTIA. ($Str + S'$).—It is of very sparing solubility, 1 part requiring 3840 of hot, and 4000 of cold water, for its solution; it is therefore thrown down whenever sulphuric acid or soluble sulphates are added to solutions of strontia. When heated with charcoal, its acid is decomposed, and *sulphuret of strontium* is formed, which affords nitrate by the action of nitric acid. This process, as practised upon sulphate of baryta, is sometimes adopted to obtain the salts of strontia, and, through them, pure strontia. Sulphate of strontia dissolves in hot sulphuric acid, but is thrown down upon adding water. At a very high heat it fuses into an opaque enamel. According to Moretti, its acid is expelled at a red heat by arsenic acid. It consists of

				Vauquelin.	Stromeyer.	Klaproth.
Strontia	1	52	56.52	54	57	58
Sulphuric acid	1	40	43.48	46	43	42
Sulphate of strontia	1	92	100.00	100	100	100

Native Sulphate of Strontia is sometimes of a blue tint, and has hence been called *celestine*. Sometimes it is colourless and transparent. Its primitive form is a prism of $104^{\circ} 48'$ and $75^{\circ} 42'$ with a rhomboidal basis. It has been found at Strontian in Argyleshire; in the vicinity of Bristol; at Montmartre near Paris; in Germany, America, &c. The finest crystallized specimens are accompanied with native sulphur, from Sicily. Its specific gravity varies between 3 and 4. A *baryto-sulphate of strontia*, composed of about 3 atoms of sulphate of baryta and 7 of sulphate of strontia, is found in Upper Canada; and another variety, called *radiated celestine*, occurs at Nörden, near Hanover.

PHOSPHURET OF STRONTIUM ($str + p$) has properties analogous to those of phosphuret of barium.

HYPOPHOSPHITE OF STRONTIA has been examined by Dulong: it is a very soluble and difficultly-crystallizable salt, and is obtained by a process similar to that for forming the hypophosphite of baryta. (*Ann. de Ch. et Ph.*, ii. 142.)

PHOSPHITE OF STRONTIA.—When carbonate of strontia is dissolved in phosphorous acid, a crystallized salt is obtained on evaporation: the crystals are decomposed by warm water, and a white powder falls, which is probably a neutral phosphite. (BERZELIUS.) When solutions of chloride of strontium and chloride of phosphorus are mixed and exposed to spontaneous evaporation, crystals of phosphite of strontia are deposited: when they are heated, phosphuretted hydrogen is evolved, and phosphate of strontia formed.

PHOSPHATE OF STRONTIA ($Str + p'$) is an insoluble white salt; it is soluble in excess of phosphoric acid. It is entirely decomposed by sulphuric acid. By igniting it with charcoal, *phosphuret of strontium* is

obtained. It fuses, before the blowpipe, into a white enamel. Obtained by precipitation from nitrate of strontia, by rhombic phosphate of soda, it consists of

				Vauquelin.	Stromeyer.
Strontia	1	52	59.1	58.76	63.435
Phosphoric acid	1	36	40.9	41.24	36.565
Phosphate of strontia	1	88	100.0	100.00	100.000

SELENITE OF STRONTIA is an insoluble white powder. (BERZELIUS, *Ann. de Chim. et Phys.*, ix. 263.) There is also a difficultly-soluble *biselenite*.

CARBONATE OF STRONTIA (*Str + car'*), when artificially formed, is a white powder, soluble in 1536 parts of hot water. When strongly heated with a little charcoal-powder, it is decomposed, carbonic oxide is given off, and pure strontia remains; but it is not decomposed by heat alone. When steam is passed over it at a high temperature, it parts with its acid and becomes a hydrate. Before the oxyhydrogen blowpipe it slowly volatilizes with a red light. It is very slightly soluble by excess of carbonic acid, and the solution deposits small acicular crystals. It is composed of

				Stromeyer.	Ure.	Klaproth.
Strontia	1	52	70.3	70.313	69.8	69.5
Carbonic acid	1	22	29.7	29.687	30.2	30.5
Carbonate of strontia	1	74	100.0	100.000	100.0	100.0

Native Carbonate of Strontia or *Strontianite* is a rare mineral. It has a greenish tint, and occurs in radiated masses, and sometimes in acicular and hexaëdral crystals. It was first discovered, in 1787, at Strontian in Argyleshire, whence the name of this earth; it has also been found in Saxony, and in Peru. Its specific gravity is 3.6. It generally contains traces of carbonate of lime.

CYANURET OF STRONTIUM has not been examined.

SULPHOCYANURET OF STRONTIUM forms delicate prismatic crystals, which deliquesce on exposure.

BORATE OF STRONTIA was formed by Dr. Hope. It is a white powder soluble in 130 parts of water.

PROPERTIES OF THE SALTS OF STRONTIA.—There is in many respects a resemblance between strontia and baryta, which has led to confusion in analysis. They are both found native in the states of sulphate and carbonate only; both sulphates are slightly soluble in excess of sulphuric acid, nearly insoluble in water, and decomposable by similar means, as well as the native carbonates; they are both crystallizable from their hot aqueous solutions, and both attract carbonic acid. The carbonates are each soluble with effervescence in most of the acids; but the native carbonates are not so easily acted on as the artificial. Pure ammonia precipitates neither one nor the other. The following are essential distinctions. Baryta and all its salts, except the sulphate, are poisonous. The corresponding strontitic salts are not so. Baryta tinges flame yellow; strontia, red. Strontia has less attraction for acids than baryta; hence

the strontitic salts are decomposed by baryta. The greater number of the barytic salts are less soluble than those of strontia; this even applies to the sulphates, for the sulphate of strontia is sensibly soluble in water, which the sulphate of baryta is not; hence the use above alluded to of an aqueous solution of sulphate of strontia as a test for barytic salts. The two classes of salts also differ in their respective forms. Pure baryta, moreover, is ten times more soluble in water than pure strontia. Baryta and strontia may also be distinguished by the following process:—Dissolve in hydrochloric, nitric, or any other acid with which it forms a soluble salt, then add excess of solution of sulphate of soda, filter, and test the clear fluid by carbonate of potassa: if any precipitate falls, the earth was strontia; if none, baryta. This again shows the slight solubility of sulphate of strontia, and the insolubility (in such solution) of sulphate of baryta. Succinate of ammonia, and fluosilicic acid, precipitate baryta, but not strontia.

§ VII. MAGNESIUM.

SIR H. DAVY found that when moistened magnesia is negatively electrized with mercury, the resulting amalgam decomposes water, and gives rise to the formation of *magnesia*. The metallic base of magnesia had not, however, been examined, till Bussy, in 1830, obtained it by the decomposition of *chloride of magnesium* by potassium. (*Ann. de Ch. et Ph.*, XLvi.) To effect this, some globules of potassium are put into a glass tube, and fragments of anhydrous chloride of magnesium placed over them: the latter is then heated till it begins to fuse, and the potassium allowed to run through it by slightly inclining the tube; ignition ensues, and the mass, when cold, affords, on washing with water, a number of small metallic globules, of a silver colour and lustre, and hard but malleable. They are not acted upon by cold water. Mixed with chloride of potassium and fused, they coalesce into one mass, their fusing point being apparently about that of silver. They dissolve in dilute hydrochloric, nitric, sulphuric, and acetic acids, and furnish solutions of magnesia. Heated in the air, or in oxygen, they burn vividly into magnesia. The equivalent of magnesium may be assumed as 12, (12·7 TURNER, 12 GMELIN.)

OXIDE OF MAGNESIUM. MAGNESIA. (*mag + o*), or M.—This is the only known compound of magnesium and oxygen; it is generally procured by exposing the carbonate of magnesia for some time to a red heat. Magnesia is a white insipid substance, which slightly greens the blue of violets, and reddens turmeric. But water which has been agitated with magnesia, when filtered through paper, does not produce similar effects. (HENRY.) Upon infusion of red roses or red cabbage it has a more decided alkaline reaction and changes them to green. Its specific gravity is 2·3; it is almost infusible, and nearly insoluble in water. Cold water is said to dissolve it in the proportion of between a six and seven thousandth part; whereas one part of the earth, according to Dr. Fyfe, requires for its solution 36,000 of boiling water. I once succeeded in agglutinating a small portion of this earth in the Voltaic flame, and whilst exposed to this high temperature, it was perfectly fused by directing upon

it the flame of oxygen and hydrogen. A mixture of magnesia and lime is scarcely more fusible than the pure earth. It does not absorb carbonic acid or moisture nearly so rapidly as the other alkaline earths, and scarcely any heat is produced by pouring water upon it. When thrown down from its solutions by potassa, collected upon a filter, and dried at 212° , it still retains a considerable quantity of water, amounting to about one-fourth its weight; in this state, therefore, it is a *hydrate of magnesia*. It is insoluble in solutions of potassa and soda. It forms bitter saline compounds with the acids, and is most readily distinguished from the other earths by the solubility and bitter taste of its *sulphate*: the sulphates of the other alkaline earths being tasteless, or very difficultly soluble, while those of the earths proper are sweet or astringent. The attractions of magnesia for the acids correspond, in most instances, closely with those of ammonia, which is in some cases displaced by, and in others displaces, magnesia. It may also be observed, that ammonia and magnesia produce double salts with most of the acids. Magnesia consists of

				Wollaston.	Gay Lussac.	Berzelius.
Magnesium	1	12	60	59.3	59.5	61.29
Oxygen	1	8	40	40.7	40.5	38.71
Magnesia	1	20	100	100.0	100.0	100.00

Native Hydrate of Magnesia.—This mineral was first discovered by Dr. Bruce, in the serpentine rocks of Hoboken, in New Jersey; it has also been found by Dr. Hibbert, in a vein, traversing serpentine, at Swinarness in Unst, one of the Shetland Isles. It has a greenish hue, and a soft lamellar texture. Sometimes it forms acicular crystals, and six-sided prisms. It consists of

				Bruce.	Fyfe.	Stromeyer.
Magnesia	1	20	69	70	69.75	68.35
Water	1	9	31	30	30.25	30.10
Native hydrate of magnesia	1	29	100	100	100.00	99.25

CHLORIDE OF MAGNESIUM (*mag + c*) may be obtained by passing chlorine over red-hot magnesia, mixed with a little charcoal; or more conveniently, by heating in a retort a mixture of 1 part of magnesia with 2 of sal-ammoniac; or by Liebig's method, which consists in evaporating a solution of equal parts of hydrochlorate of ammonia and hydrated chloride of magnesium, and heating the dry residue in a platinum vessel till the hydrochlorate of ammonia is expelled and the mass fuses. The residuary *chloride of magnesium* forms a lamellar white crystalline mass, which evolves heat when acted on by water. This chloride cannot be obtained by merely evaporating its aqueous solution to dryness in an open vessel, for in that case hydrochloric acid escapes, and magnesia remains; but Davy found that magnesia heated in chlorine absorbed it, and gave out the usual relative volume of oxygen. Chloride of magnesium is very deliquescent; it is soluble in half its weight of water, and in twice its weight of alcohol. It consists of

Magnesium	1	12	25
Chlorine	1	36	75
Chloride of magnesium	1	48	100

When solution of chloride of magnesium is concentrated by evaporation, and exposed to a cold atmosphere, it yields prismatic hydrated crystals, deliquescent, very soluble in water and alcohol, and of a bitter and biting taste. This salt was formerly termed *muriate of magnesia*; it is found in a few saline springs, and in the water of the ocean forming the principal ingredient in the liquid which remains after the separation of sea-salt, and which is usually called *bittern*. The above-mentioned crystals consist, according to Thomson, of

Chloride of magnesium	1	48	47.2
Water	6	54	52.8
<hr/>			
Crystals of hydrated chloride of magnesium	1	102	100.0

SEA-WATER.—Chloride of sodium is as already stated by far the most abundant ingredient in the waters of the ocean; it constitutes in fact about two-thirds of the whole saline contents; the magnesian salts are however very characteristic of sea-water, and confer upon it many of its peculiarities, such especially as its bitter flavour and clamminess; sulphate of lime is the predominant calcareous salt. An accurate analysis of sea-water, made with the precision with which many mineral waters have been examined, is at present a desideratum in chemistry. As far as the above-mentioned salts are concerned, the following are the average contents of a pint of sea-water:—

Chloride of sodium	180.5 grs.
Chloride of magnesium	23
Sulphate of magnesia	15.5
Sulphate of lime	7.1
	<hr/>
	226.1

According to Murray (*Edin. Phil. Trans.*, viii. 205), the elements of these salts, *previous to evaporation*, are arranged thus:—

Chloride of sodium	180.5 grs.
Chloride of magnesium	18.3
Chloride of calcium	5.7
Sulphate of magnesia	21.6
	<hr/>
	226.1

The average specific gravity of *sea-water* is 1.026 or 1.028. It freezes at about 28.5°, and does not appear materially to differ in composition in different latitudes, provided it be taken from a sufficient depth. Near the mouths of rivers, and in the vicinities of melting ice or snow, its composition will of course vary. Traces of chloride of potassium, and of iodine and bromine, may also be found in it; and, according to Dr. Marcet (*Phil. Trans.*, 1819 and 1822), of triple sulphate of magnesia and potassa, and of hydrochlorate of ammonia. He has also detected in it a minute portion of carbonate of lime. In respect to the general constitution of sea-water, it appears from Marcet's researches, (1.) That the southern ocean contains more salt than the northern, in the ratio of 1.02919 to 1.02757. (2.) That the mean specific gravity of sea-water near the equator is 1.02777, or intermediate between that of the northern and southern hemispheres. (3.) That there is no notable difference in sea-water under different meridians. (4.) That there is no satisfactory evidence that the sea at great depths is more salt than at the surface.

(5.) That the sea in general contains most salt where it is deepest and most remote from land, and that its saltness is always diminished in the vicinity of large masses of ice. (6.) That small inland seas, though communicating with the ocean, are much less salt than the ocean. (7.) That the Mediterranean contains rather larger proportions of salt than the ocean. (PROUT, *Bridgewater Treatise*.)

CHLORIDE OF MAGNESIA.—The fluid obtained by condensing chlorine in a mixture of magnesia and water, was recommended by Davy (*Elem. of Chem. Phil.*, 243) for some delicate bleaching-operations, but it has not been generally employed.

CHLORATE OF MAGNESIA is obtained by mixing a solution of fluosilicate of magnesia with a hot saturated solution of chlorate of potassa, as long as a precipitate falls. (BERZELIUS.) When formed by saturating chloric acid with carbonate of magnesia, it is bitter, difficultly crystallizable, deliquescent, and very soluble in water. From the analysis of Chenevix (*Phil. Trans.*, 1802), the crystals appear to contain 2 atoms of water; the constitution of the salt being $(M + C' + 2Q)$.

AMMONIO-CHLORIDE OF MAGNESIUM is a crystallizable salt soluble in 6 parts of water at 60° .

POTASSO-CHLORIDE OF MAGNESIUM may, by very careful evaporation, be obtained in rhombic crystals; but the constitution of this salt is so delicate, that it is liable to be separated into chloride of potassium and of magnesia by water alone; and it is with certainty decomposed by alcohol, which takes up the magnesian chloride, and leaves the other undissolved. (MARCET, *Phil. Trans.*, 1822, p. 456.)

IODIDE OF MAGNESIUM. (*mag + i*.)—When iodine is heated with magnesia and water, *iodide of magnesia* and *iodate of magnesia* are formed. By concentrating the solution, both salts are partly decomposed, and a brown flocculent *iodide of magnesia* falls (resembling kermes in appearance), which, when heated, loses part of its iodine, and is changed into a *subiodide*. (HENRY, i. 593.) The hydrated iodide obtained by dissolving magnesia in hydriodic acid is very difficultly crystallized, and when heated gives off hydriodic acid and leaves magnesia.

BROMIDE OF MAGNESIUM (*mag + b*) is only known as a bitter deliquescent *hydrate*, resolved, by heat and air, into magnesia and hydrobromic acid. It forms acicular prisms, very soluble in water and alcohol. It probably exists in very minute quantity in sea-water.

FLUORIDE OF MAGNESIUM (*mag + f*) is obtained by digesting magnesia in hydrofluoric acid. Berzelius says that it is insoluble, and undecomposed at a red heat.

NITRATE OF MAGNESIA crystallizes with difficulty in rhomboidal prisms, deliquescent, and soluble in its weight of water. In pure alcohol it is nearly insoluble, but 1 part dissolves in about 9 of alcohol of the specific gravity .840. Its taste is cooling and bitter, and it is decomposed at a red heat. It is sometimes found in crude nitre. The crystallized salt, according to Kirwan and Bergman, contains about 30 per cent. of

water; according to Thomson, 6 atoms. According to Graham, 1 atom of water is essential to the constitution of this salt, so that when the crystals containing 6 atoms of water are highly heated, only 5 atoms go off, and 1 atom remains in combination; this monohydrate may be fused without decomposition; when intensely heated the salt loses both acid and water, and magnesia remains: he therefore represents this salt as $(M + n' + q) + 5q$. On evaporating the alcoholic solution of nitrate of magnesia, a solid alcoate is formed with which a portion of water is also probably associated.

AMMONIO-NITRATE OF MAGNESIA may be obtained by evaporating a mixed solution of nitrate of ammonia and nitrate of magnesia; it forms prismatic crystals, of a bitter acid taste, soluble in about 11 parts of water at 60° , and less deliquescent than their component salts separately. (FOURCROY, *Ann. de Ch.*, iv. 215.) Berzelius admits the existence of this salt, but Graham did not succeed in forming it, or any other double nitrate.

SULPHURET OF MAGNESIUM. (*mag* + *s*.)—Sulphur and magnesia do not appear to form a complete sulphuret, for when melted together the compound does not dissolve in water; and when heated, the sulphur burns off. Nor can a sulphuret of magnesium be obtained by heating the metal with sulphur. Berzelius states that sulphate of magnesia decomposed by an aqueous solution of sulphuret of barium yields a precipitate of sulphate of baryta and a solution of sulphuret of magnesium. According to Berthier, when sulphate of magnesia is intensely heated in a crucible lined with charcoal, a sulphuret of magnesium is formed; but when the charcoal is mixed with the sulphate, sulphur is evolved, and magnesia only remains. Hydrogen passed over sulphate of magnesia at a high temperature would also probably give this sulphuret.

HYPOSULPHITE OF MAGNESIA ($M + \bar{s}$) may be formed by boiling sublimed sulphur in solution of sulphite of magnesia; it is bitter, very soluble, but not deliquescent. Being more soluble in hot than cold water, it readily crystallizes as its solution cools; heated, sulphur escapes, but it is not very combustible.

SULPHITE OF MAGNESIA ($M + \bar{s}$) is prepared by passing sulphurous acid through water containing diffused magnesia. It forms tetraëdral crystals soluble in 20 parts of water at 60° , of a sweetish and sulphurous taste; they become opaque in the air, but are very slowly converted into sulphate: when in solution, however, this change soon ensues. When heated, this salt softens and acquires the consistence of gum, losing 0.45 of its weight; at a high heat the acid is disengaged, and pure magnesia remains. (DUMAS.)

AMMONIO-SULPHITE OF MAGNESIA may be obtained by mixing the solution of the two salts, or by saturating acid sulphite of magnesia with ammonia. It forms transparent difficultly-soluble crystals.

HYPOSULPHATE OF MAGNESIA ($M + \bar{s}'$) is difficultly crystallizable in hexagonal prisms, intensely bitter, fusible in their water of crystallization, very soluble in water, but not deliquescent. It is formed by mixing

the solutions of sulphate of magnesia and hyposulphate of baryta, and appears from Heeren's analysis (POGGENDORFF, vii. 179), to consist, when crystallized, of

Magnesia	1	20	13·70
Hyposulphuric acid	1	72	49·31
Water	6	54	36·99
<hr/>			
Crystallized hyposulphate of magnesia	1	146	100·00

SULPHATE OF MAGNESIA is a commonly-occurring salt, much used in medicine as an aperient. When concentrated sulphuric acid is poured upon magnesia, intense heat is produced, and sometimes light. If the acid be dilute, and poured upon carbonate of magnesia, the latter is slowly dissolved with effervescence; and, upon evaporating the filtered solution, crystals of sulphate of magnesia may be obtained.

The commercial demands for sulphate of magnesia are chiefly supplied from two sources, namely, sea-water, and magnesian limestone. When sea-water is resorted to, the greater part of the common salt is first removed by evaporation, and the remaining *bittern*, consisting chiefly of a solution of chloride of magnesium and sulphate of magnesia, is boiled down with the addition of sulphuric acid, by which the chloride is ultimately decomposed and converted into sulphate. Or the bittern may be decomposed by hydrate of lime, which is mixed with it in tanks, and the resulting precipitate is afterwards neutralized by sulphuric acid, by which sulphate of magnesia and sulphate of lime are obtained. When magnesian limestone is used as a source of sulphate of magnesia it is calcined, and reduced to powder by sprinkling it with water; it is then diffused through water and neutralized by sulphuric acid, and as sulphate of magnesia is so much more soluble than the sulphate of lime, it is easily separated. A solution of sulphate of lime may also be decomposed by carbonate of magnesia, as is sometimes seen, where water holding sulphate of lime in solution filters through strata of magnesian limestone.

The sulphate of magnesia from bittern is generally preferred as a source of magnesia, or carbonate of magnesia, in consequence of the absence of iron, traces of which are always discoverable in the sulphate obtained from the magnesian limestones; but as the latter is free from chloride of magnesium, and consequently not deliquescent, and may be obtained very nearly pure, it is preferred for general medical uses.

There are some saline springs or mineral waters in which sulphate of magnesia is the leading ingredient, as those of Seidlitz, Seydschutz. Egra, and formerly those of Epsom in Surrey, whence the name of *Epsom salt*: it is also largely obtained in some alum works: it not unfrequently occurs as a fine capillary incrustation upon the damp walls of cellars and new buildings; and it has been found *native*, constituting the *hair salt* of mineralogists.

Sulphate of magnesia crystallizes (see fig. 10, p. 112) in four-sided prisms with reversed dièdral summits, or four-sided pyramids. They refract double. (BROOKE, *Ann. of Phil.*, 2nd series, vi. 40.) Their density is 1·76. Exposed to the air, it has, when pure, a slight tendency to efflorescence, but the salt of commerce is often deliquescent from the presence of a little chloride of magnesium. Its taste is saline and bitter. It is

soluble in its own weight of water at 60° , and in three-fourths its weight of boiling water; or, more correctly, 100 parts of water at 32° dissolve 25.76 parts of the anhydrous salt, and for every degree above that temperature they take up 0.26564 parts additional. (GAY LUSSAC.) When exposed to heat it readily loses 6 equivalents of its water of crystallization, but retains 1 equivalent more obstinately. At a red heat it becomes anhydrous, and at a higher temperature it runs into a white enamel.

The aqueous solution of sulphate of magnesia furnishes a precipitate of hydrated carbonate upon the addition of the carbonates of potassa and soda, but carbonate of ammonia does not even render it turbid, unless heat be applied, in which case a precipitate is also thrown down. The alkaline bicarbonates occasion no precipitate when added to cold solution of sulphate of magnesia, but after some hours crystals of hydrated carbonate of magnesia are deposited.

The sulphate of magnesia of commerce is occasionally adulterated with small crystals of sulphate of soda; the fraud is detected by the inferior weight of the precipitate occasioned by adding carbonate of potassa; 100 grains of pure crystallized sulphate of magnesia furnishing a precipitate weighing, when dried at 212° , about 40 grains. Anhydrous sulphate of magnesia consists of

				Gay Henry.	Lussac.	Ber- zelius.	Wenzel.
Magnesia	1	20	33.33	32.14	33	34	35.5
Sulphuric acid	1	40	66.67	67.86	67	66	64.5
Anhydrous sulphate of magnesia	1	60	100.00	100.00	100	100	100.0

And the *crystallized* salt contains, according to Graham, 1 atom of constituent water and 6 of water of crystallization, it being represented by $(M + S' + Q) + 6Q$. The proximate elements of the crystals are

				Gay Lussac.	Wenzel.
Magnesia	1	20	16.26	16.04	16.86
Sulphuric acid	1	40	32.52	32.53	30.64
Water	7	63	51.22	51.43	52.50
Crystallized sulphate of magnesia	1	123	100.00	100.00	100.00

AMMONIO-SULPHATE OF MAGNESIA may be obtained by mixing solution of sulphate of ammonia with solution of sulphate of magnesia; or by pouring ammonia into a solution of the sulphate of magnesia, in which case, part only of the magnesia is thrown down, the remainder forming, with the sulphate of ammonia, this triple salt. It crystallizes in oblique rhombic prisms, (BROOKE, *Ann. of Phil.*, 2nd series, vii. 117,) consisting of

			Mitscherlich.		Fourcroy.
Ammonia	1	17	9.00	Sulphate of	} . . . 32
Magnesia	1	20	10.58	ammonia	
Sulphuric acid	2	30	42.33	Sulphate of	} . . . 68
Water	8	72	38.09	magnesia	
Crystallized	1	189	100.00	Dry	100

SULPHATE OF POTASSA AND MAGNESIA $(P + M + 2S') + 6Q$ forms rhomboidal crystals, scarcely more soluble than sulphate of potassa, and of a bitter taste. This salt appears, from Dr. Marcet's observations, to exist in sea-water. It may be obtained by evaporating a mixture of 2 parts

of sulphate of potassa, and 1 of sulphate of magnesia, in complex crystals. According to Mr. Graham's views of the constitution of these sulphates, the atom of constituent water in this salt is replaced by an atom of sulphate of potassa; its components being

Potassa . . .	1	. . .	48	. . .	Mitscherlich.	23.46
Magnesia . . .	1	. . .	20	. . .		9.94
Sulphuric acid	2	. . .	80	. . .		39.76
Water . . .	6	. . .	54	. . .		26.84
	<hr/> 1		<hr/> 202			<hr/> 100.00

SULPHATE OF SODA AND MAGNESIA ($S + M + 2S'$) + 6 *q* forms truncated rhombic crystals, soluble in about 3 parts of water at 60°; it was first examined by Link, and afterwards by Dr. Murray, (*Edin. Phil. Trans.*, viii.) In this salt an atom of sulphate of soda replaces the constituent atom of water in the sulphate of magnesia; for its proximate elements are

Sulphate of soda . . .	1	. . .	72	. . .	Murray.	38.7	. . .	39
Sulphate of magnesia . . .	1	. . .	60	. . .		32.3	. . .	32
Water	6	. . .	54	. . .		29.0	. . .	29
	<hr/> 1		<hr/> 186			<hr/> 100.0		<hr/> 100

PHOSPHURET OF MAGNESIUM has not been examined.

HYPOPHOSPHITE OF MAGNESIA may be obtained by boiling oxalate of magnesia for a long time with hypophosphite of lime, filtering, and carefully evaporating the liquid. It crystallizes in octoëdra, containing 55 *per cent.* of water of crystallization: when this salt is heated it gives off water and phosphuretted hydrogen, and phosphate of magnesia remains.

PHOSPHITE OF MAGNESIA is precipitated, according to Fourcroy and Vauquelin, by adding phosphite of potassa to sulphate of magnesia, in the form of white flocks soluble in 400 parts of water, and by spontaneous evaporation yielding tetraëdral efflorescent crystals. According to Dumas, phosphite of magnesia can only be obtained by the direct combination of magnesia and phosphorous acid; evaporated in vacuo, it forms crystalline films containing much more water of crystallization than the phosphates of baryta or lime: when decomposed by heat it yields hydrogen and phosphuretted hydrogen, and a yellowish-brown phosphate of magnesia remains. An *ammonio-phosphite of magnesia* may be formed, which is crystallizable, and difficultly soluble.

PHOSPHATE OF MAGNESIA. This salt may be obtained by dissolving magnesia in phosphoric acid and evaporating till it crystallizes. It may also be formed by adding phosphoric acid to a solution of acetate of magnesia, and evaporating the mixture. According to Fourcroy, four-sided prismatic crystals of phosphate of magnesia may be obtained by mixing the aqueous solutions of phosphate of soda and sulphate of magnesia. They require about 15 parts of water at 60° for solution, and are slowly efflorescent: when heated before the blowpipe, they leave a fusible transparent glass. They are resolved by boiling water into an insoluble *subphosphate of magnesia* and a soluble *superphosphate*. According to

Graham, "phosphate of magnesia is formed by mixing cold solutions of common phosphate of soda and of sulphate of magnesia, and allowing the liquid to stand for 24 hours: the salt appears in tufts of slender prisms which effloresce in dry air; they are soluble in about 100 times their weight of water. The composition of this salt, which I carefully examined, may be expressed by the following formula: $\text{HO}, 2\text{MgO}, \text{PO}_5 + 2\text{HO} + 12\text{HO}.$ " (*Phil. Trans.*, 1837.) The crystallized *neutral phosphate of magnesia* consists, according to Riffault, of

				Riffault.
Magnesia	1	20	16.8	} . . 47
Phosphoric acid	1	36	30.2	
Water	7	63	53.0	
Crystallized phosphate of magnesia	1	119	100.0	100

The mineral called *Wagnerite* appears to be a sesquiphosphate of magnesia, but it also contains fluorine.

PHOSPHATE OF AMMONIA AND MAGNESIA.—This double salt is produced when an ammoniacal salt or pure ammonia is added to a mixture of common phosphate of soda with any magnesian salt. Thus on adding ammonia or carbonate of ammonia to a mixed solution of phosphate of soda and sulphate of magnesia, the ammonio-magnesian phosphate falls in the form of a white granular or crystalline precipitate, insoluble in the liquid from which it is thrown down, but sparingly soluble in pure water, so that it cannot be washed upon the filter without sensible loss. It is readily soluble in the greater number of diluted acids. When its solution in aqueous carbonic acid is exposed to the air it slowly forms a superficial crystalline film as the carbonic acid escapes; and if bicarbonate of ammonia be used in its formation it falls slowly, but its appearance is curiously accelerated by drawing lines with a glass rod upon the surface of the glass or basin containing the mixed solutions, when the double phosphate presently appears upon those lines. This method of recognising the presence of magnesia was first suggested by Wollaston; and indeed, the formation of this double salt is the readiest test of magnesia which we possess. The composition of this salt has been variously stated, especially as regards the proportion of ammonia and of water which it retains under various modes of drying. According to Graham, when dried at 65° it is a compound (in our equivalents) of 2 atoms of phosphoric acid, 2 of magnesia, 1 of ammonia, and 13 of water; of this water, it is assumed, that 1 atom is in combination with the ammonia, constituting oxide of ammonium; that is $(n + 4h + o)$. At 212° , 10 atoms of the remaining 12 atoms of water may be expelled without any loss of ammonia. If it be rapidly dried and then raised to a red heat, it appears to burn like tinder and leaves a residue of pyrophosphate of magnesia, which contains 36.6 per cent. of magnesia. Adopting Mr. Graham's view of the constitution of this salt, it is a compound of 2 atoms of oxide of magnesium, 1 of oxide of ammonium, 2 of phosphoric acid, 2 of constituent water, and 10 of water of crystallization; and the following, therefore, is its rational formula: $2(\text{mag} + o) + (n + 4h + o) + 2(p + 2o) + 2(h + o) + 10(h + o)$. Its proximate components are—

Magnesia	2	40	16.3
Ammonia	1	17	6.9
Phosphoric acid	2	72	29.3
Water	13	117	47.5
Ammonio-magnesian phosphate	1	246	100.0

The ammonio-magnesian phosphate is deposited from human urine, often in the form of white sand, or as a superficial crystalline film, especially in cases where the natural acidity of the urine is diminished by diet, medicine, or morbid action, constituting what has been termed the phosphatic diathesis: it frequently forms urinary calculi both in the human subject and in quadrupeds, and it commonly occurs in intestinal concretions; it is found in the grain of wheat, barley, and rye, and when ammonia is added to fresh beer this salt is precipitated.

CARBONATE OF MAGNESIA.—This term is generally applied to the white precipitate obtained by adding carbonate of soda or potassa to a solution of sulphate of magnesia, and thoroughlyedulcorating and drying the precipitate; it is usually obtained from boiling solutions, and great attention should be paid to the purity of the water employed in washing the precipitate, and to the method of drying it. It varies somewhat in composition, and in density, when dried, according to the method adopted in its precipitation. It is the *magnesia alba* of pharmacy, and appears to be a compound of hydrate of magnesia and carbonate of magnesia, probably in the proportions of 1 atom of quadrihydrate and 1 atom of carbonate. $(M + 4q) + (M + car')$, or, perhaps, $(M + 3q) + (M + car' + q)$. It has been repeatedly analyzed, and the following are some of the results:—

	Dalton and				Bucholz.		Berzelius.
	Kirwan.	Bergman	Henry.	Klaproth.	hot ppt.	cold ppt.	
Magnesia	45	45	43	40	42	33	41.60 to 43.2
Carbonic acid	34	25	40	33	35	32	36.53 to 36.4
Water	21	30	17	27	23	35	21.82 to 20.4
	100	100	100	100	100	100	100.00 100.0

Two kinds of carbonate of magnesia are kept in the shops, the *light* and the *heavy*: they are prepared as follows. (PEREIRA, *Elements of Mat. Med.*, 363.) “For *heavy* magnesia, add 1 volume of a cold saturated solution of carbonate of soda to a boiling mixture of 1 volume of a saturated solution of sulphate of magnesia and 3 volumes of water: boil until effervescence has ceased, constantly stirring with a spatula. Then dilute with boiling water, set aside, pour off the supernatant liquor, and wash the precipitate with hot water on a linen cloth; afterwards dry it by heat in an iron pot. *Light* magnesia is prepared by employing dilute solutions of the sulphate of magnesia and carbonate of soda. If no heat be used it is apt to be gritty. A heavy and gritty magnesia is prepared by separately dissolving 12 parts of sulphate of magnesia and 13 parts of crystallized carbonate of soda in as small a quantity of water as possible, mixing the hot solutions, and washing the precipitate.”

When a current of carbonic acid gas is passed through a mixture of water and magnesia, a clear solution of *carbonate of magnesia* is obtained, which has a bitter taste, and which, when surcharged with carbonic acid,

affords a useful medicinal preparation. But a solid or crystallized bicarbonate of magnesia cannot be obtained, and the crystals which are deposited when this solution is left to spontaneous evaporation, and which are oblique rhombic prisms (BROOKE, *Ann. of Phil.*, 2nd series, vi. 375), are hydrated carbonate of magnesia, composed of

						Berzelius.	Henry.
Magnesia . . .	1	. . .	20	. . .	29	. . .	29·6 . . . 30
Carbonic acid .	1	. . .	22	. . .	32	. . .	31·5 . . . 30
Water	3	. . .	27	. . .	39	. . .	38·9 . . . 40
	1		69		100		100·0 . . . 100

When these crystals of hydrated carbonate are put into cold water they are decomposed, carbonate of magnesia is dissolved, and a subcarbonate is deposited. Boiling water produces the same precipitate, but carbonic acid is evolved, and nothing remains in solution; in this case the precipitate is *magnesia alba*. (BERZELIUS.) Exposed to a dry air they effloresce and lose 2 equivalents of water. (GRAHAM.)

There are other processes than those above mentioned by which the carbonate of magnesia of commerce is procured, such as by decomposing the *bittern* of the sea-salt works, by magnesian limestone, or by crude carbonate of ammonia, produced by the distillation of bone; in the latter case sulphate and hydrochlorate of ammonia and carbonate of magnesia result; the solution of the ammoniacal salts is evaporated to dryness and sublimed with chalk; carbonate of ammonia is thus reproduced for the decomposition of a second portion of *bittern*, and so on.

Native Carbonate of Magnesia has been found in Piedmont and Moravia, constituting the mineral called *magnesite*. It has also been found at Hoboken, in North America, in veins in a serpentine rock, accompanying the *native hydrate*. It is generally white and friable, and in some places in fine acicular crystals. A variety of *native carbonate of magnesia* brought from the East Indies by Mr. Babington, has been described and analyzed by Dr. Henry (*Ann. of Phil.*, i. 254). It is white, massive, hard, of a conchoidal fracture, and translucent at the edges; specific gravity 2·6. It slowly dissolves in acids, and is composed of 1 atom of magnesia + 1 atom carbonic acid.

CARBONATE OF AMMONIA AND MAGNESIA.—When 3 parts of sesquicarbonate of ammonia and 1 of sulphate of magnesia are dissolved, transparent rhomboëdral crystals are after a time deposited, constituting this double salt. They are soluble without decomposition in boiling water, but continued boiling renders the solution turbid. At a red heat their carbonic acid, ammonia, and water are volatilized, and magnesia amounting to 15·6 per cent. remains. (GUIBOUT.)

CARBONATE OF POTASSA AND MAGNESIA.—When excess of bicarbonate of potassa is mixed with chloride of magnesium no precipitation ensues, but in a few days crystals are formed, of an alkaline taste, which are decomposed by hot water. They may be regarded as a hydrated compound of 1 atom of bicarbonate of potassa + 2 atoms of carbonate of magnesia, for they consist of—

				Berzelius.
Potassa . . .	1	48	18.7	18.28
Magnesia . . .	2	40	15.6	15.99
Carbonic acid . .	4	88	34.2	34.49
Water . . .	9	81	31.5	31.24
	<hr/> 1	<hr/> 257	<hr/> 100.0	<hr/> 100.00

CARBONATE OF SODA AND MAGNESIA is formed as the triple potassa salt, by bicarbonate of soda; but it is not so easily decomposed; and, accordingly, when magnesia is precipitated by excess of carbonate of soda, a portion of the triple soda-salt is retained, and not easily washed away.

CARBONATE OF LIME AND MAGNESIA is the mineral known under the name of *bitter-spar*; it has the primitive form of carbonate of lime, and consists of 1 atom of each of its component carbonates.

BORATE OF MAGNESIA may be formed artificially, by boiling boracic acid and magnesia in water; as the solution cools, it deposits the salt in crystalline grains. Wöhler obtained a neutral borate of magnesia by heating the mixed solutions of sulphate of magnesia and borate of soda to the boiling point, to form a precipitate; this was then allowed to digest for some time in the mother-liquor at a temperature nearly as low as 32°, by which it was redissolved, and acicular crystals subsequently formed upon the sides of the vessel, which were insoluble in water. When heated, these crystals lost 52.5 per cent. of water, = 8 atoms, and left a compound of single equivalents of boracic acid and magnesia. After the separation of this neutral borate, the liquid afforded large crystals of a double borate of soda and magnesia, containing 52.5 per cent. of water. Borate of magnesia occurs native in a mineral called *boracite*, hitherto only found in the duchy of Luneburgh. Its primitive form is the cube, but the edges and angles are generally replaced by secondary planes, and four of the angles are always observed to present a greater number of facets than the other four: these crystals become electric by heat, the most complex angles being rendered positive, and the simplest negative. It sometimes contains lime. It appears to consist of

				Arfwedson.	Stromeyer.
Magnesia . 1½	30	30.61	30.3	33	
Boracic acid 1	68	69.39	69.7	67	
<hr/> Boracite 1	<hr/> 98	<hr/> 100.00	<hr/> 100.0	<hr/> 100	

THE SALTS OF MAGNESIA are, for the greater part, soluble in water, and of a bitter taste; they afford precipitates of carbonate of magnesia, upon the addition of carbonate of potassa or soda: they are not precipitated by the alkaline bicarbonates. Phosphate of soda occasions no immediate precipitate when added to a magnesian salt, but the subsequent addition of ammonia causes a white precipitate of the ammonio-magnesian phosphate. A solution of phosphate of ammonia with excess of base is also, upon the same principle, a good precipitant of magnesian salts. The pure magnesian salts, when heated before the blowpipe with a little nitrate of cobalt, furnish pale rose-coloured compounds.

The separation of magnesia and lime is a problem of some importance in analytical chemistry, as they often exist together in the same mineral, more especially in the varieties of magnesian limestone. When solution

of carbonate of ammonia is added to the mixed solution of lime and magnesia in nitric or hydrochloric acids, carbonate of lime falls, and the magnesia is retained in solution, and may be separated by boiling with carbonate of potassa: this method, however, is not susceptible of accuracy, for a portion of carbonate of lime is retained with the magnesia in solution, and an ammonio-magnesian salt is also formed. Mr. R. Phillips (*Quarterly Journ.*, vi. 317) proposes the following process:—"To the hydrochloric or nitric solution of lime and magnesia, add sulphate of ammonia in sufficient quantity; evaporate the mixture gradually to dryness, and then heat the residue to redness till it ceases to lose weight, by the volatilization of the hydrochlorate or nitrate of ammonia formed: note the weight of the mixed salt, reduce it to powder, and wash it with a saturated solution of sulphate of lime till all the sulphate of magnesia appears to be dissolved; dry the sulphate of lime left, and by deducting its weight from that of the mixed sulphates, the quantity of magnesia dissolved will appear." Another process is as follows:—"To the mixed solution of lime and magnesia add oxalate of ammonia slightly acid, collect the precipitate, wash, and dry it at 212° : 100 parts indicate between 38 and 39 of lime. If nitric acid were used for solution, the magnesia may afterwards be obtained by evaporation and heating the residue to redness in a platinum crucible till it ceases to lose weight. If sulphuric acid were the solvent, the same operation affords dry sulphate of magnesia, of which 60 parts are equivalent to 20 magnesia; or the magnesia may, in other cases, be precipitated by phosphate of ammonia as above stated (p. 713). In the analysis of minerals which contain magnesia, and which resist the action of acids, fusion with alkaline bodies must be resorted to. As instances of these analyses the reader is referred to Klaproth's examination of the *chrysolite*, and of *olivine*, in the 7th and 8th sections of the first volume of his *Analytical Essays*. See also ROSE's *Analytical Chemistry*.

MAGNESIAN MINERALS are generally soft and apparently unctuous to the touch; they have seldom either lustre or transparency, and are generally more or less of a green colour. *Steatite* or *soapstone*, *talc*, and *asbestos*, may be taken as instances. The *chrysolite* however contains more than half its weight of magnesia. The mineral called *bitterspar*, of which the finest specimens come from the Tyrol, contains 45 *per cent.* carbonate of magnesia, 52 carbonate of lime, and a little iron and manganese. Its primitive crystal is a rhomboid nearly allied to that of carbonate of lime; its angles being $106^{\circ} 20'$, and $73^{\circ} 80'$. It is generally of a yellowish colour, and a pearly lustre; semi-transparent and brittle. A variety found at *Miemo* in Tuscany, has been called *Miemitite*. The species of marble, termed *Dolomite*, found in the Alps, at Icolmkill in Scotland, and elsewhere, contains also a large quantity, generally 40 *per cent.* of carbonate of magnesia. The same may be said of the *magnesian limestone* of Derby and Nottingham: it is generally of a yellowish colour, and less rapidly soluble in dilute hydrochloric acid than the pure limestone, whence the French have termed it *chaux carbonatée lente*. The lime which it affords is much esteemed for cements, but for agricultural purposes it is often mischievous, in consequence of its remaining caustic for a very long time, and thus injuring the young plant.

§ VIII. MANGANESE.

THE common ore of manganese is the black, or *peroxide*, which is found in considerable abundance, and is of important use in the arts; this metal also occurs in a few animal products, and is not uncommonly discovered in the ashes of vegetables. Particular attention was first directed to the black oxide of manganese by Scheele, in 1774, and shortly afterwards Gahn found that it contained a peculiar metal, which he first called *magnesium*, but which was afterwards termed *Manganese*.

In some respects manganese resembles the metals already described; in others, it is eminently different. Like them, it has a powerful affinity for oxygen, speedily attracting it from air and water; and its oxides are extremely difficult of decomposition: they have, however, nothing in common with alkaline bodies; and manganese, in its highest state of oxidizement, constitutes an acid.

To obtain metallic manganese, the *carbonate of manganese* may be mixed into a paste with oil, and subjected to heat gradually raised to redness, in a glass or earthen retort, or other close vessel. The carbonaceous mixture thus obtained is then rammed into a good crucible, which is filled up with charcoal-powder, and subjected for two hours to the strong white-heat of a wind-furnace: a metallic button is thus obtained, which is manganese, containing a little carbon and silicium, from which it may be freed, according to Dr. John, by fusion with borax in a crucible coated with charcoal; it is doubtful, however, as Berzelius has observed, whether in this case it does not contain a little boron.

When the *tartrate of manganese and potassa* is intensely heated in a wind-furnace, it furnishes globules of metallic manganese; and as this salt is easily obtained in a state of purity, its decomposition is perhaps the simplest process for obtaining the pure metal, care being taken to exclude foreign substances derivable from the fuel or from the crucible.

Manganese, as thus obtained, is a hard gray metal, exhaling a peculiar odour when handled or breathed upon; it is brittle, and has a granular and sometimes a slightly crystalline fracture; its specific gravity is 8.013 according to John, 7.05 according to Berthier, and 6.8 according to Bergman. The specific heat of a specimen of manganese, not however pure, but containing carbon, was, as determined by Regnault, = 0.14411. When pure, it does not affect the magnetic-needle, but often does so from containing a trace of iron. It is softer than cast-iron, and admits of filing, yet brittle enough to be reduced into an iron-gray metallic powder. It is best preserved in naphtha; for in the air it soon tarnishes and crumbles down into a black powder, and undergoes the same change in water, with the evolution of hydrogen gas. It may also be conveniently kept in a small glass tube hermetically sealed. When handled with moist fingers it exhales a disagreeable odour, and when acted on by the acids the purest specimens hitherto obtained always afford traces of carbon; there are therefore considerable discrepancies in the accounts of the properties ascribed to this metal.

The equivalent of manganese may be assumed as = 28, (28.5 Gmelin, 27.7 Turner.)

MANGANESE AND OXYGEN.—Five compounds of manganese and oxygen, three of which are oxides, and two acids, are now generally admitted; together with two intermediate oxides, namely, the red oxide, and the mineral called Varvicite. The formulæ of these several compounds are as follows:—

Protoxide	(<i>man</i> + <i>o</i>)
Sesquioxide or deutoxide	(<i>man</i> + $\frac{11}{2}$ <i>o</i>) or ($2\text{ }man + 3\text{ }o$)
Binoxide or peroxide . .	(<i>man</i> + $2\text{ }o$)
Red oxide	($3\text{ }man + 4\text{ }o$) or (<i>man</i> + <i>o</i>) + ($2\text{ }man + 3\text{ }o$)
Varvicite	($2\text{ }man + 3\frac{1}{2}\text{ }o$) or (<i>man</i> + $\frac{11}{2}$ <i>o</i>) + (<i>man</i> + $2\text{ }o$)
Manganic acid	(<i>man</i> + $3\text{ }o$)
Permanganic acid . . .	(<i>man</i> + $3\frac{1}{2}\text{ }o$) or ($2\text{ }man + 7\text{ }o$)

PROTOXIDE OF MANGANESE. MANGANOUS OXIDE. (*man* + *o*) or MAN, is obtained: (1.) By passing a current of hydrogen over the pure deutoxide or peroxide of manganese, contained in a porcelain or iron tube, exposed to a heat gradually raised to bright redness: water is formed, and a dingy-green powder remains in the tube, which is the *protoxide*. The oxide obtained by igniting the protonitrate of manganese is recommended by Turner as best suited to this reduction, the native oxide and especially the peroxide being reduced with great difficulty. The reduction, he says, commences at a low red-heat, but a full red-heat is required for its completion. (2.) It may also be procured by mixing the peroxide with half its weight of hydrochlorate of ammonia, and projecting the mixture in successive portions into a red-hot crucible; the product is lixiviated, and the solution of chloride of manganese, thus obtained, is decomposed by the addition of carbonate of potassa; the precipitate is collected, washed, dried, and exposed, out of the contact of air, to an intense heat: or it may be heated in a tube, through which a current of hydrogen is passed. In this process, so long as there is excess of the oxide, the manganese only is converted into chloride by the hydrochlorate of ammonia, and other metals that may be present are not rendered soluble. (3.) Wöhler and Liebig obtain it by fusing chloride of manganese with twice its weight of carbonate of soda; the resulting chloride of sodium is removed by washing from the residuary protoxide of manganese. The addition of a small quantity of hydrochlorate of ammonia in this process is useful to prevent the formation of any peroxide.

Protoxide of manganese is of a gray-green colour, and when obtained by means of hydrogen at a low temperature acquires oxygen from the air, and is sometimes pyrophoric: obtained by the other processes it is not altered by mere exposure to air. Heated in the air, it absorbs oxygen, and is converted into deutoxide; and at a temperature of about 600° burns like tinder. It is soluble in the dilute acids, and is the basis of the ordinary manganesian salts. When put into concentrated sulphuric acid, it evolves intense heat. Its solutions and salts are nearly colourless when perfectly pure, but they generally acquire a slightly-pink hue, probably from the presence of a minute quantity of manganic acid. When ammonia is added to the solutions of this oxide, the whole is not precipitated, but it forms a triple salt, as is the case with magnesia. If manganic solutions contain silica, (as is often the case, and especially

in the analysis of ores and minerals containing manganese,) the silica falls in combination with the oxide of manganese, when they are precipitated by an alkali; it may be separated by dissolving the moist precipitate in hydrochloric acid, evaporation to dryness, and washing. (BERZELIUS.) The equivalent number of manganese deduced from the composition of this oxide is 28, and it consists of

				Berzelius and		
				Forchhammer.	Arfwedson.	Davy.
Manganese	1	28	77.77	76.5	73.07	79
Oxygen	1	8	22.23	23.5	21.93	21
Protoxide of manganese	1	36	100.00	100.0	100.00	100

HYDRATED PROTOXIDE OF MANGANESE.—When the solution of chloride of manganese is decomposed by a solution of potassa, a bulky white precipitate falls, which is a *hydrated protoxide* of manganese, containing, according to Davy, 24 per cent. of water; it very speedily becomes brown by exposure to air, in consequence of the absorption of oxygen; and, when collected and washed upon a filter, it becomes a brown powder, which is a hydrate of the deutoxide.

SESQUIOXIDE OF MANGANESE. DEUTOXIDE OF MANGANESE. (*man* + 110.)—When protoxide, or carbonate of manganese, is exposed for some time to a red heat in an open vessel, it absorbs oxygen, and is converted into a deep-brown powder. An oxide similarly constituted is also obtained by heating the pure peroxide of manganese in a platinum crucible till it ceases to give out oxygen. When ammonia is added to the pink solution obtained by triturating a mixture of peroxide of manganese and binoxalate of potassa with water, a precipitate is obtained, which, when well washed and heated red-hot, is similar in composition to the above. By exposing the protonitrate of manganese to a red heat, the sesquioxide remains in the form of a black powder. The characters of this oxide, in respect to solvents, differ with its state of aggregation; but it does not form permanent or definite salts; for such of its acid solutions which are at first red, become colourless when heated, or when exposed to air and light, and deposit peroxide, while a portion of protoxide remains in solution. Heated with hydrochloric acid, chlorine is evolved, and with sulphuric acid, oxygen; and a protochloride and protosulphate of manganese result. Digested with nitric acid, a protonitrate and peroxide of manganese are formed. “From the proportion of oxygen and manganese in this oxide, it has sometimes been regarded as a compound of 1 equivalent of peroxide and 1 of protoxide: in that case, it would be constituted like a salt, and should have the properties of that class of compounds; but Mitscherlich has succeeded in combining it with sulphuric acid, and has obtained with it an alum similar in form and constitution to those of peroxide of iron and alumina; it must therefore be considered as a direct compound of 2 equivalents of manganese and 3 of oxygen.” (TURNER.) Assuming it as a sesquioxide, it contains

				Forchhammer.	Arfwedson and Berzelius.
Manganese	1	28	70	70.4	72.74
Oxygen	1½	12	30	29.6	27.26
Sesquioxide of manganese	1	40	100	100.0	100.00

HYDRATED SESQUIOXIDE OF MANGANESE is obtained by exposing the moist protoxide to the action of air. It is a common natural product (the *manganite* of mineralogists), occurring crystallized and massive, and so closely resembling the peroxide, that it is often difficult to distinguish them; the powder of the hydrated sesquioxide is, however, generally *brown*, that of the peroxide *black*; the former, heated in a tube, gives off water and little oxygen; the latter, little moisture and much oxygen. Heated by the blowpipe with glass of borax, the sesquioxide of manganese dissolves with a red or violet colour in the outer flame; in the inner flame it becomes colourless in consequence of deoxidization, but reacquires colour when transferred to the outer oxidizing flame.

BINOXIDE OF MANGANESE. PEROXIDE OF MANGANESE. (*man* + 2 O.) —This is the oxide which most commonly occurs *native*, and is resorted to as the source of the other combinations of this metal. In this country it is common in Devonshire, Somersetshire, and Aberdeenshire. It is found in a variety of forms: compact and massive, pulverulent and crystallized. Many of the latter varieties have a gray metallic lustre, and are found acicularly radiated, and in rhomboidal prisms. Its specific gravity varies between 4·8 and 4·9. It is the *pyrolusite* of some mineralogists. The following analyses of five samples of native peroxide of manganese are given by Dumas, upon the authorities of Berthier (1. 2. 3.), Klaproth (4.), and Turner (5.).

	I.	II.	III.	IV.	V.
Peroxide of manganese	93·8	84·0	72·7	99·5	97·8
Peroxide of iron	1·0	2·0	1·0	0·0	0·0
Oxide of copper	trace	trace	trace	0·0	0·0
Carbonate of lime	0·0	9·0	24·0	0·0	0·0
Silica	4·0	4·0	1·2	0·0	0·5
Baryta	0·0	0·0	0·0	0·0	0·5
Water	1·2	1·0	1·1	0·5	1·2
	100·0	100·0	100·0	100·0	100·0

Under the name of *manganese*, this substance is met with in commerce, and is largely consumed in the manufacture of bleaching compounds. In the laboratory, it is resorted to as a source of oxygen gas, for which purpose it should be well dried previous to introducing it into the retort (p. 358). Sometimes it is mixed with carbonaceous matter, and then yields carbonic acid: it also generally gives off a little nitrogen upon the first application of heat, the source of which is not obvious. Carbonate of lime, sulphate of baryta, oxide of iron, and several other substances, are frequently associated with it. It is also used to give a black colour to earthenware, to remove the brown colour which glass derives from peroxide of iron, and sometimes to sweeten foul water at sea, or to prevent its becoming so. It usually loses weight, on being dried at a temperature not exceeding 300°; at a red heat it becomes *sesquioxide*; and, intensely heated in an iron tube, or with a minute quantity of carbonaceous matter, part of it becomes *protoxide*. It is not altered by air or water. It forms no combinations with the acids; but such of them as appear to dissolve it, reduce it to the state of protoxide. Gently heated with hydrochloric acid, chlorine is liberated, in consequence of the decomposition of the acid by the oxygen of the oxide (p. 399). Boiled with sulphuric acid, oxygen

is evolved, and a soluble *sulphate of the protoxide* is formed, together with a small portion of *manganic acid*, which gives the solution a pink colour and bleaching properties. Nitric acid does not attack it unless it contains sesquioxide, or some deoxidizing agent be at the same time present. Peroxide of manganese consists of

				Forchhammer.	Berzelius and Arfwedson.
Manganese	1	28	63.6	63.75	64.02
Oxygen	2	16	36.4	36.35	35.98
Peroxide of manganese	1	44	100.0	100.00	100.00

HYDRATED PEROXIDE OF MANGANESE is obtained, according to Berthier, by passing chlorine through the protocarbonate of manganese diffused in water; a black powder falls, which, when washed and carefully dried, consists of 88 peroxide and 12 water. A hydrated peroxide (consisting of 1 atom of peroxide and 1 of water) is formed by precipitating protochloride of manganese by chloride of lime. The soft black mineral known to our miners under the name *Wad*, is also a hydrate of the peroxide of manganese: it contains 2 atoms of water. Dr. Thomson states that when a neutral solution of protoxide of manganese is mixed with a solution of chloride of soda, made by adding carbonate of soda to a solution of neutral chloride of lime till the lime is all precipitated, a beautiful black precipitate falls, which, when washed and dried, consists of 3 atoms of binoxide and 1 of water.

Pure peroxide of manganese is sometimes useful as a test of the presence of iodine, bromine, and chlorine. When mixed with a salt containing iodine, and the mixture heated with a little sulphuric acid, the violet vapour of iodine is evolved; the salts of bromine give in the same way a brown vapour; and from the chlorides chlorine is evolved.

RED OXIDE OF MANGANESE.—This is the *oxidum manganoso-manganicum* of Berzelius and Arfwedson: it exists native, constituting the mineral termed *Hausmanite*, which appears to contain 3 atoms of manganese and 4 of oxygen: proportions which are equivalent to 1 atom of protoxide and 2 atoms of sesquioxide, or 2 atoms of protoxide and 1 of peroxide. The processes are very uncertain by which this oxide is stated to be produced artificially: according to some, it is formed by exposing the peroxide or sesquioxide to a *white* heat, either in close or open vessels; or it is said to be produced when any oxide of manganese is heated strongly in the air; but in these cases, mixtures of the oxides of manganese, as above stated, rather than any definite oxide, are the results: the following are the atomic equivalents, showing the different views which may be taken of this oxide, regarding it either as a definite oxide, or as a mixture of others:—

Manganese 3	84	or	Protoxide 1	36	or	Protoxide 2	72
Oxygen 4	32		Sesquioxide 2	80		Peroxide 1	44
Red oxide 1	116			116			116

VARVICITE.—A peculiar oxide of manganese was discovered by Mr. Phillips among some manganese ores from Hartshill, in Warwickshire, to which, from its locality, he gave the above name. Professor Turner

afterwards detected it in the manganese of Ilefeld, in the Hartz. It is harder, and has more lustre, and a more decidedly lamellated texture than the common peroxide: its density is 4.531. It has not been found regularly crystallized, but some of the Hartz specimens yield it in pseudo-crystals, having the form of six-sided pyramids of calcareous spar. When strongly heated, it is converted into red oxide, losing 5.725 per cent. of water, and 7.385 of oxygen. These proportions are represented by 2 atoms of manganese and $3\frac{1}{2}$ of oxygen, or 1 atom of the sesquioxide and 1 of the peroxide.

Manganese .	2	.	.	56		Sesquioxide .	1	.	.	40
Oxygen .	$3\frac{1}{2}$.	.	28	or	Peroxide .	1	.	.	44
	$\frac{1}{1}$			84			$\frac{1}{1}$			84

And in Varvicite 2 atoms of oxide (84×2) = 168, are combined with 1 of water = 9, giving for Varvicite the equivalent $168 + 9 = 177$. (*Phil. Mag. and Ann.*, v. vi. and vii.)

MANGANIC ACID. MANGANESIC ACID.—When peroxide of manganese is heated to redness with nitrate of potassa, a compound is obtained, which, when put into water, furnishes a solution exhibiting various tints of green, purple, and red, and which was therefore called *Chameleon mineral*. A similar compound is more perfectly obtained by fusing the peroxide with caustic potassa at a red heat, which furnishes a green substance when the alkali is in excess, but black if the oxide predominate; the former gives a green, the latter a pink solution, both of which when duly diluted exhibit various changes of tint, and ultimately become colourless, with the deposition of a brown powder. It was stated by Chevallot and Edwards, in 1818, that this compound could not be obtained in close vessels, but that, air being present, oxygen was absorbed, and on evaporating the pink solution, they obtained crystals, which they regarded as a salt of potassa with manganic acid. Frommherz succeeded in obtaining manganic acid as follows:—2 parts of nitrate of baryta are mixed with 1 of peroxide of manganese, and exposed to a red heat; a green mass is obtained, which is to be reduced to fine powder, mixed with 25 parts of water, and a stream of carbonic acid passed through the mixture, which is kept constantly stirred; carbonate of baryta is formed, and a deep violet-coloured solution of manganic acid. When the diffused powder has lost its green colour, the fluid is poured clear off, and boiled for a quarter of an hour to expel excess of carbonic acid, during which a portion of carbonate of baryta and of peroxide of manganese are precipitated: the clear fluid is boiled down to one-fourth its bulk, again left to become clear, and ultimately evaporated to a small bulk: during this evaporation, oxide of manganese is again separated, in consequence of the decomposition of a part of the acid; but the residuary solution forms on cooling acicular crystals of *hydrated manganic acid* (containing 8.5 per cent. of water). All attempts have failed to deprive this acid of water. Its solution has a peculiar astringent taste, possesses considerable bleaching powers, (hence *chlorine* has often been erroneously suspected in these solutions,) and exhibits a violet colour by transmitted light, but appears of a carmine-red by reflected light: it tinges the skin brown. It is decom-

posed by boiling, especially when diluted; and also by exposure to the sun's rays.

Chlorine has no effect on manganic acid, but iodine decomposes it, and becomes iodic acid. It is decomposed by hydrogen, sulphur, and phosphorus, by the hydracids, and by carburetted hydrogen and carburet of sulphur, and all organic substances: hence it cannot be filtered, being decomposed by the paper; it oxidizes the metals. With potassa, soda, baryta, and strontia, it forms definite salts.

According to Mitscherlich manganic and sulphuric acids are isomorphous, and the manganates are isomorphous with the sulphates and also with the chromates. The elements of manganic acid are

					Unverdorben.	Frommherz.	Mitscherlich.				
Manganese .	1	. .	28	. .	53·8	. .	58·74	. .	59·45	. .	54
Oxygen . .	3	. .	24	. .	46·2	. .	41·26	. .	40·55	. .	46
Manganic acid	1		52		100·0		100·00		100·00		100

MANGANATE OF POTASSA.—The following process is given by Dr. Gregory for the preparation of this salt. Mix 4 parts of finely-powdered peroxide of manganese with $3\frac{1}{2}$ of chlorate of potassa, and add them to 5 parts of hydrate of potassa dissolved in a small quantity of water. The mixture is evaporated to dryness, powdered, and then ignited in a platinum crucible, but not fused, at a low red-heat. Digested in a small quantity of cold water this affords a deep green solution of the alkaline manganate, which may be obtained in crystals of the same colour by evaporating the solution over sulphuric acid in the air-pump. (GRAHAM, *Elem. of Chem.*, 537.)

PERMANGANIC ACID. HYPERMANGANIC ACID.—It is supposed by Mitscherlich, that the salt obtained by adding peroxide of manganese to fused chlorate of potassa, (WÖHLER, POGGENDORFF, xxvii. 626,) contains manganese in the highest state of oxidizement, that is, combined with 3·5 atoms of oxygen; but the exact composition of the green, pink, and purple salts cannot be considered as satisfactorily ascertained.

When permanganate of baryta is decomposed by an equivalent of sulphuric acid, a solution of permanganic acid is obtained of a deep red colour, but which, like manganic acid, is extremely prone to change; its decomposition is very rapid at 212° , oxygen is given out, and hydrated peroxide of manganese subsides; organic substances, such as paper, cork, or linen, also determine its immediate change. It has considerable bleaching power, a property referable to the evolution of nascent oxygen (or to aqueous solution of oxygen, or oxywater). According to Huenefeld permanganic acid may be obtained in more permanent hydrated crystals by washing manganate of baryta with hot water, which resolves it into peroxide of manganese and permanganate of baryta: he decomposed the latter salt by phosphoric acid, and washed out the liberated permanganic acid, evaporated its solution to dryness, and obtained a reddish brown crystalline mass. When this was fused with anhydrous sulphuric acid, and then further heated in a retort, a crimson sublimate in acicular crystals was obtained, being apparently a compound of sulphuric and permanganic acids. (BERZELIUS.) It would appear from this statement that in those cases where the permanganic acid is speedily decomposed, some foreign

substance, probably organic, has been present. In this acid the elements are combined in the ratio of 2 equivalents of manganese and 7 of oxygen; it must, therefore, be considered as a compound of

Manganese . . .	1	. . .	28	. . .	50
Oxygen	$3\frac{1}{2}$. . .	28	. . .	50
<hr/>					
Permanganic acid	1		56		100

The peculiar green tint obtained by heating compounds of manganese with potassa, is usefully resorted to as a ready means of recognising that metal before the blowpipe. It has often been stated that pink solutions, obtained by certain acids from the peroxide, contain the sesquioxide; but some experiments, in reference to this subject, made by Mr. Pearsall, in the laboratory of the Royal Institution, render it probable that the appearance of a pink colour is always indicative of the presence of manganic acid. (*Royal Instit. Journ.*, Aug. 1831, p. 49.)

PERMANGANATE OF AMMONIA is obtained by the double decomposition of permanganate of potassa by fluosilicate of ammonia: the solution is deep purple, and furnishes crystals of the same colour on evaporation. (LIEBIG.)

PERMANGANATE OF POTASSA.—To obtain this salt boiling water is poured on manganate of potassa, hydrated peroxide of manganese subsides, and a beautiful pink solution of permanganate of potassa is obtained, which should be rapidly concentrated by distillation, all organic matter being rigidly excluded; on cooling crystals of a very intense purple are obtained, which according to Mitscherlich are isomorphous with perchlorate of potassa. They deflagrate upon charcoal, and detonate with phosphorus. When boiled in dilute nitric acid oxygen is evolved, and hydrated peroxide of manganese separates.

PROTOCHLORIDE OF MANGANESE. (*man + c.*)—Metallic manganese burns in chlorine. When peroxide of manganese is heated with hydrochlorate of ammonia, as above directed (p. 719), a solution of *chloride of manganese* is easily obtained from the residue, which, if evaporated by a gentle heat, furnishes transparent pinkish crystals, soluble in water and alcohol. The same salt is obtained by dissolving carbonate of manganese in dilute hydrochloric acid.

When peroxide of manganese is boiled in hydrochloric acid, as in the common process for evolving chlorine, a solution of chloride of manganese more or less contaminated by iron is obtained, from which a pure chloride may be procured by boiling it down to expel excess of acid, diluting it with water and again boiling with the addition of carbonate of manganese, by which the whole of the peroxide of iron is precipitated. If about one-fourth of the impure solution of chloride of manganese be reserved, and precipitated by carbonate of soda, a quantity of carbonate of manganese will be obtained sufficient to precipitate the iron from the other three-fourths of the liquid, and which may be used for that purpose after it has been washed. The absence of iron in the solution is ascertained by its yielding a white precipitate without any shade of blue, by ferrocyanuret of potassium; it may then be evaporated to dryness, or the chloride of manganese may be crystallized in its hydrated form. (EVERITT.)

Exposed, out of the contact of air, to a heat gradually raised to redness, the crystals lose water, to the amount of about 40 per cent., and leave a lamellar *anhydrous chloride of manganese*; heated in the contact of air, this chloride is decomposed and converted into an oxide, as is the case with the corresponding chloride of magnesium. The anhydrous salt combines according to Brandes with 4 equivalents of water, to form the hydrated crystals; it loses 3 of these and retains 1 when dried at 212° , and at a red heat this last equivalent escapes. 100 parts of water dissolve 38.3 of the anhydrous chloride at the temperature of 50° , 46.2 parts at 88° , and 55 parts at 144° . A higher temperature, instead of increasing, diminishes its solubility. (BRANDES.) Absolute alcohol dissolves half its weight of the anhydrous chloride of manganese, and affords by evaporation in vacuo a crystalline *alcoate* containing 2 equivalents of alcohol. (GRAHAM.) Chloride of manganese consists of

				J. Davy.	Arfwedson.
Manganese	1	28	43.7	46	44.25
Chlorine	1	36	56.3	54	55.75
Chloride of manganese	1	64	100.0	100	100.00

PERCHLORIDE OF MANGANESE has been described by Dumas; it is formed by adding fused chloride of sodium to a sulphuric solution of permanganic acid; the compound passes off in the form of a green vapour, condensable at 0° into an olive-coloured liquid. If the vapour be conveyed into a moistened flask it acquires a red tint, and hydrochloric and permanganic acids are generated. The simplest process for preparing it consists in forming a green chameleon-mineral by fusing peroxide of manganese with potassa, and pouring dilute sulphuric acid upon it, by which a permanganate and sulphate of potassa are obtained. By the affusion of strong sulphuric acid these salts yield a solution of permanganic acid, to which small pieces of fused common salt are added, as long as green vapour is evolved. (*Edin. Journ. of Science*, viii. 179.) From the phenomena of its formation and decomposition, this chloride is supposed to consist of 1 atom of manganese and $3\frac{1}{2}$ of chlorine: it corresponds, therefore, to the permanganic acid.

AMMONIO-CHLORIDE OF MANGANESE is a soluble and crystallizable salt, not decomposed by excess of ammonia.

CHLORATE OF MANGANESE has not been examined.

IODIDE OF MANGANESE, as formed by the action of hydriodic acid on protoxide of manganese, is a soluble colourless compound. (GMELIN.) The *iodate* has not been examined; nor has the bromide or bromate.

FLUORIDE OF MANGANESE is formed, according to Dumas and Wöhler (*Edinburgh Journal of Science*, ix.), by mixing the green chameleon-mineral with half its weight of pure fluor-spar in fine powder, and decomposing the mixture in a platinum vessel by anhydrous sulphuric acid: a vapour, of a deeper tint than chlorine, is evolved, which acquires a red colour on mixture with atmospheric air, and gives with water a red solution of hydrofluoric and manganic acids. It is decomposed by the contact of glass, fluosilicic acid is formed, and a brown powder deposited, which appears to be anhydrous manganic acid. This fluoride probably consists of 1 proportional of manganese and 3 of fluorine. When car-

bonate of manganese is digested in hydrofluoric acid, amethyst-coloured crystals may be obtained by evaporation, probably of *hydrated protofluoride of manganese*.

NITRATE OF MANGANESE. ($MAN + N'$).—Dilute nitric acid readily dissolves protoxide of manganese, and forms a *protonitrate*, which may be obtained by evaporation in vacuo, in prismatic crystals, deliquescent, very soluble in water and in alcohol, and of a bitter taste; their alcoholic solution burns with a green flame. The same salt may be obtained by digesting peroxide of manganese in nitric acid with a portion of gum or sugar, which abstracts oxygen, carbonic acid is evolved, and the protoxide dissolved by the acid. Exposed to light, the solution of the protonitrate lets fall a portion of peroxide of manganese. When dilute nitric acid is poured upon the deutoxide of manganese, a protonitrate and peroxide are formed.

The crystals consist, according to Thomson, of

Protoxide of manganese	1	36	23.5
Nitric acid	1	54	35.3
Water	7	63	41.2
<hr/>			
Crystallized protonitrate of manganese	1	153	100.0

SULPHURET OF MANGANESE. ($man + S$).—When dried protosulphate of manganese is ignited with one-sixth its weight of finely-powdered charcoal, or when a current of sulphuretted hydrogen is passed over the protosulphate heated to redness, a true *sulphuret of manganese* is obtained. (BERTHIER, *Ann. de Ch. et Ph.*, xxiv. 273; ARFWEDSON, *Ann. of Phil.*, vii. 332.) It has a gray metallic lustre. It is perfectly soluble in dilute sulphuric and hydrochloric acid, with the evolution of sulphuretted hydrogen gas. It is identical with the *native* sulphuret of manganese, a rare ore, found in Cornwall and Transylvania. Sulphuret of manganese consists of

		Dobereiner.		Arfwedson	
		<i>Artificial.</i>		<i>Native.</i>	
Manganese	1	28	63.6	65.86	63.13
Sulphur	1	16	36.4	34.14	36.87
<hr/>		<hr/>		<hr/>	
Sulphuret of manganese	1	44	100.0	100.00	100.00

When sulphur is heated with peroxide of manganese, sulphurous acid is evolved, and a greenish substance obtained, which also appears to be a compound of manganese and sulphur, and not a sulphuretted oxide. It is also thrown down from solutions of the protoxide by the alkaline hydrosulphurets in the form of an orange-coloured hydrate; which when heated evolves water, and becomes the sulphuret. When hydrogen is passed over protosulphate of manganese at a red heat an *oxysulphuret* is produced.

When a solution of protosulphate of manganese is mixed with a solution of carburet of sulphur in caustic potassa, a gray precipitate falls, which, when stirred so as to bring it to the surface, assumes a fine purple colour: this gradually disappears, and the precipitate assumes the red or orange colour of sulphurets of manganese. (BERZELIUS.)

HYPOSULPHITE OF MANGANESE ($MAN + S$) remains in solution when sulphate of manganese is decomposed by hyposulphite of lime. It has not been further examined.

SULPHITE OF MANGANESE ($\text{MAN} + \text{S}$) is obtained by passing sulphurous acid through a mixture of carbonate of manganese and water till the carbonic acid is expelled. It is a white granular tasteless powder, insoluble in water and in alcohol, and not altered by exposure to air. It dissolves in excess of sulphurous acid, and is decomposed by heat. (BERZELIUS.)

HYPOSULPHATE OF MANGANESE. ($\text{MAN} + \text{S}'$).—When peroxide of manganese (previously digested in nitric acid, and thoroughly washed, to deprive it of hydrated oxide) is diffused through water, and sulphurous acid passed into it, a neutral hyposulphate of the protoxide is obtained. It affords a deliquescent salt on evaporation. (See p. 475.)

SULPHATE OF MANGANESE ($\text{MAN} + \text{S}'$) is formed by dissolving the protoxide or protocarbonate in dilute sulphuric acid, and evaporating; it may also be obtained by mixing peroxide of manganese into a paste with sulphuric acid, and heating it in a basin nearly to redness; oxygen is evolved, and the dry mass washed with water affords the sulphate. This salt is much used in dyeing and calico-printing, for which purpose Mr. Graham states that it is prepared by “igniting peroxide of manganese mixed with about one-tenth its weight of pounded coal in a gas retort. The protoxide thus formed is dissolved in sulphuric acid with the addition at the end of a little hydrochloric acid; the sulphate is evaporated to dryness, and again heated to redness in the gas retort; the iron is found, after the ignition, in the state of peroxide, and insoluble, the persulphate of iron being decomposed, while the sulphate of manganese is not injured by the temperature of ignition, and remains soluble. The solution is of an amethystine colour, and does not readily crystallize. When cloth is passed through sulphate of manganese and afterwards through a caustic alkali, protoxide of manganese is precipitated upon it and rapidly becomes brown in the air; or it is at once peroxidized by passing the cloth through a solution of chloride of lime. The colour thus produced is called *manganese brown*.”

Sulphate of manganese, as usually obtained by evaporation from the neutral solution, forms rhombic prisms which contain 4 atoms of water. When the crystals are formed between 45° and 68° , they contain 5 equivalents of water, and are isomorphous with sulphate of copper; and when formed under 42° they include 7 atoms of water, and are isomorphous with sulphate of iron. For these curious facts we are indebted to Mitscherlich; and lastly, when a concentrated solution of sulphate of manganese is mixed with sulphuric acid, it yields on evaporation small granular crystals containing only 1 atom of water. The solubility of sulphate of manganese varies with its water of crystallization; but, according to Brandes, the anhydrous salt is soluble in 2 parts of water at 60° , and in its own weight at 122° ; at a higher temperature its solubility diminishes. It is insoluble in alcohol. The taste of sulphate of manganese is styptic and bitterish, and the crystals have generally a slight tinge of pink, probably from a trace of permanganic acid. At 240° , they lose 3 atoms of water, but retain 1 until heated above 400° ; at a red heat the salt becomes anhydrous and in that state consists of

Protoxide of manganese	1	36	47.4
Sulphuric acid	1	40	52.6
<hr/>			
Anhydrous protosulphate of manganese	1	76	100.0

AMMONIO-SULPHATE OF MANGANESE is a soluble and crystallizable salt, obtained when sulphate of ammonia and sulphate of manganese are mixed in atomic proportions. Its crystals contain 8 proportionals of water, and are of a pale rose-colour. According to H. Rose 100 parts of anhydrous sulphate of manganese absorb 45·30 of dry ammonia, forming a white bulky powder: the ammonia escapes by exposure to air or heat.

POTASSA-SULPHATE OF MANGANESE forms colourless crystals, containing 6 atoms of water. (BERZELIUS.) According to Thomson the crystals have a fine flesh-red colour, the same shape as those of the ammonio-sulphate of magnesia, and contain 5 atoms of water.

PHOSPHURET OF MANGANESE (*man + p*) is of a blue-white metallic lustre, and considerably inflammable: it is permanent in the air, brittle, and easily fused. (PELLETIER, *Ann. de Ch.*, xiii. 137.)

PHOSPHITE and HYPOPHOSPHITE OF MANGANESE have not been examined.

PHOSPHATE OF MANGANESE (*MAN + p'*) is precipitated in the form of a white nearly insoluble powder, by adding phosphate of soda to sulphate of manganese. Berzelius observes, that in analyses this salt is difficultly distinguished from phosphate of lime and phosphate of magnesia. It is, however, decomposed by boiling with caustic potassa, and the oxide assumes a dark colour.

CARBURET OF MANGANESE. (*man + car.*)—When the metal reduced from its oxide is heated with charcoal, it often assumes a lamellated appearance, from combining with that element. Carburet of manganese is also not uncommonly met with in combination with carburet of iron in some varieties of cast iron.

CARBONATE OF MANGANESE (*MAN + car!*) is white, or pale-red, insipid, and insoluble in water. It is precipitated as a hydrate, by alkaline carbonates, from the protochloride or protosulphate. When heated it loses water and becomes brown. It is found *native*, constituting the *spathose ore of manganese*, which is anhydrous. When the artificial carbonate is carefully dried at 100° it probably consists of

Protoxide of manganese	1	.	.	36	.	.	53·73	.	.	Forchammer.
Carbonic acid	1	.	.	22	.	.	32·84	.	.	51·755
Water	1	.	.	9	.	.	13·43	.	.	33·050
	1			67			100·00			93·325

CYANURET OF MANGANESE falls in the form of a gray insoluble precipitate, when solution of cyanuret of potassium is added to a protosalt of manganese. The precipitate is soluble in excess of the precipitant. (BERZELIUS.)

When cyanuret of manganese is dissolved in cyanuret of potassium, the solution yields on evaporation brown acicular crystals which are very easily decomposed. (L. GMELIN.)

SULPHOCYANURET OF MANGANESE is a colourless soluble salt. It is almost insoluble in absolute alcohol.

BORATE OF MANGANESE ($\text{MAN} + \text{bo}'$) is precipitated in the form of a white powder when solution of borate of soda is mixed with protosulphate of manganese. If the salt of manganese be mixed with a salt of magnesia, borax occasions no precipitate, and the borate is itself soluble in sulphate of magnesia. (BERZELIUS.)

CHARACTERS OF THE SALTS OF MANGANESE.—The salts of manganese, containing the protoxide, are mostly soluble in water: the solution is colourless or slightly pink, of a bitterish astringent taste, and often becomes turbid and brown by exposure to air. They are not precipitated by sulphuretted hydrogen, by hydriodic acid, or by tincture of galls; they furnish white precipitates with the alkalis, which soon become discoloured by exposure to air. The alkaline carbonates throw down white precipitates, which gradually assume a hue of purple; they are precipitated white by ferrocyanuret of potassium, and orange or reddish-brown by hydrosulphuret of ammonia. Ammonia only throws down half the oxide, and forms a triple salt with the remainder; or, if there be excess of acid, the triple salt only is formed, and there is no precipitation. Manganese is not thrown down in the metallic state by any of the other metals. The sulphate and the chloride are used in calico-printing.

Before the blowpipe, *oxide of manganese* gives, with microcosmic salt, in the exterior flame, a fine amethyst colour, which disappears in the interior flame. With borax it gives a yellowish or reddish glass. When the manganese, from its combination with iron, or any other cause, does not produce a sufficiently intense colour in the glass, a little nitre may be added to it while in a state of fusion, and the glass then becomes dark-violet while hot, and reddish-violet when cool: it is not reduced.

§ IX. IRON.

THE most important native combinations of iron, whence the immense supplies for the arts of life are drawn, are the *oxides*: it is also found combined with sulphur, and with several acids; it is so abundant that there are few fossils free from it. It is found in small quantity in some animal and vegetable bodies; and in several mineral waters. The alchemists distinguished it by the name and symbol of Mars ♂. It has been known from a very remote period, and was employed in the time of Moses for cutting-instruments.

Iron is a metal of a blue-white colour, fusible at a white heat, and with great difficulty when it is perfectly pure and free from oxygen, sulphur, and carbon. Its texture varies with the method of working it; in bars or wire it appears longitudinally fibrous, but when it has been long kept at a red heat it acquires a crystalline texture and has a tendency to cuboidal fracture. Its specific gravity is 7.77 to 7.8. Its specific heat is 0.11379. (REGNAULT.) Upon the same authority the specific heat of cast-steel is 0.11848, and that of cast iron 0.12728. It is extremely ductile, but cannot be hammered out into very thin leaves. It is very tenacious; and at a bright-red heat is pliable, and admits of being *welded* or joined by hammering to another piece of the red-hot metal. It is attracted by the magnet, but does not retain magnetism when perfectly pure; and at a bright-red heat becomes perfectly indifferent to it.

Native Iron.—Iron, in a state approaching purity, is found among the grains of platinum from the Uralian mines, and a thin vein of it is said to have been discovered in chlorite slate near Canaan in the United States of America. The term *native iron* is usually applied to the extraordinary detached masses of the metal which are of meteoric origin. In this state it is flexible, generally more or less cellular, and often contains a green substance of a vitreous appearance, which is a silicate of iron and magnesia (meteoric olivin?). It has been found in Africa and America, and in Siberia, where a mass of it, weighing 1600 lbs., was discovered by Professor Pallas. The mass found in Peru, described by Don Rubin de Celis, weighed 15 tons. In the year 1751, a mass of the same substance was seen to fall from the atmosphere in Croatia: it appeared as a large globe of fire, and is preserved in the Imperial Museum of Vienna. (See *Nickel*.)

Exposed to heat and air, iron absorbs oxygen and becomes superficially converted into a fusible oxide; when exposed to damp atmospheric air, it becomes encrusted by a brown substance called *rust*, which is also an oxide of iron. When iron is in a state of extreme mechanical division its affinity for oxygen is such that it heats and even ignites on exposure to air, and burns into an oxide; this is the case with the metal, as it is obtained by the action of hydrogen upon oxide of iron at a high temperature; it then forms a porous and highly oxidizable mass, which requires the same precautions for its preservation in the metallic state as potassium. In a dense mass, iron is not affected by dry air, and it even retains its polish when immersed in pure distilled water which has been deprived of air by long boiling; but in common water, or in water exposed to air, it soon rusts, more especially where it is in contact both of air and water; and in these cases the change is often very rapid, in consequence of the presence of carbonic acid. The oxidizement of iron by water is effectually prevented by the presence of the alkalis; and in lime water, or in a weak solution of potassa or soda, the metal keeps its lustre for years; but all acid or even neutral salts appear to have an opposite effect. By the contact of zinc, iron is also protected from oxidizement and corrosion, in consequence of the electro-negative state into which it is then thrown (p. 313); hence the advantage of zinced iron in general, and especially of zinced iron plate, in all cases where the preservation of iron is to be ensured. In deep water, according to E. Davy, a black and not a red oxide is formed; and in sea water iron is often converted into a substance somewhat resembling plumbago; but these changes generally refer to cast iron or other impure forms of the metal, and are frequently referable to voltaic action.

OXIDES OF IRON.—Iron is susceptible of two definite degrees of oxidizement, forming a *protoxide* and a *peroxide*: in the former, 1 atom of iron is combined with 1 of oxygen, but in the latter, 1 atom of iron is combined with $1\frac{1}{2}$ oxygen, so that it is in fact a *sesquioxide*. Both these oxides are salifiable, giving rise to ferrous and ferric salts. There also exists a definite native combination of these oxides, forming the *magnetic iron ore*; the *oxidum ferroso-ferricum* of some writers; and a similar compound may be formed by various artificial operations; it is commonly called the *black oxide of iron*.

PROTOXIDE OF IRON. FERROUS OXIDE. ($fe + o$) or Fe .—When a solution of potassa or soda is dropped into a solution of pure protosulphate of iron a white precipitate falls, which, however, speedily changes colour, and in the contact of air passes through various shades of green, then becomes bluish black, from which it gradually passes into brown: these changes arise from the absorption of oxygen; but the white precipitate which first appears is the *hydrated protoxide*; when boiled in water under the cautious exclusion of air it becomes black, probably from the loss of its combined water; but if collected upon a filter it exhibits the changes above described, and has not hitherto been isolated in a dry state: it is the base of the green or protosalts of iron; it is insoluble in water and in the fixed alkaline solutions: it is sparingly soluble in ammonia, and easily soluble in the greater number of the acids even when considerably diluted. The action of dilute sulphuric acid upon pure iron is attended by the formation of this oxide, in consequence of the decomposition of water; so that the hydrogen which is in this case evolved is the equivalent of the oxygen transferred to the metal, and furnishes a datum for the determination of the atomic weight of iron and of this oxide. The equivalent of iron, thus deduced, is 28 (27 GMELIN. 27.16 BERZELIUS. 27.8 STROMEYER. 28.3 GAY LUSSAC. 28 TURNER), and the protoxide consists of

			Dobereiner.		Bucholz.	Berzelius.	Gay Lussac.
Iron	1	28	77.8	76.9	77	77.62	77.94
Oxygen	1	8	22.2	23.1	23	22.38	22.06
Protoxide of iron	1	36	100.0	100.0	100	100.00	100.00

PEROXIDE OF IRON. SESQUIOXIDE OF IRON. FERRIC OXIDE. ($fe + 1\frac{1}{2}o$) or ($2fe + 3o$).—When protoxide of iron is boiled in nitric acid, and precipitated by ammonia, washed, and dried at a low red-heat, it increases in weight, and acquires a brown colour. When a solution of iron in nitrohydrochloric acid is precipitated by an alkali, a bulky brown *hydrated peroxide of iron* falls, which, when dried, assumes a deeper colour, and is *anhydrous peroxide*. When sulphate of iron is decomposed by a very high temperature, a red powder remains, which is also the peroxide, and which was formerly called *colcothar*. It is also formed by deflagrating iron-filings with nitre, and washing the residue: this constituted the *Saffron of Mars* (*Crocus Martis*) of ancient pharmacy. The colour of the peroxide of iron varies according to the mode of its formation and the temperature to which it has been subjected: it is generally a reddish or yellow-brown powder, which acquires a darkened hue by heat, and is not magnetic.

This oxide of iron is a weak base, or what has sometimes been called an *indifferent oxide*: its salts generally have a brown colour and an acid reaction, and when very dilute their solutions are decomposed by boiling, in which case the acid of the salt combines with the water and the peroxide is precipitated. In some cases this oxide even acts as an acid. It is thrown down from its solutions by ammonia, potassa, and soda, in the form of a bulky brown or orange *hydrate*, and in that state is easily redissolved by acids; but when it has been well dried and exposed to an intense heat it becomes intractable and very difficultly acted upon by the greater number of the acids, even in their concentrated state. After exposure to air it always contains traces of ammonia. When certain

organic substances are present in solutions of this oxide, they prevent its precipitation by the alkalis. This is the case with the serum of the blood, and with hot solutions of gelatin, starch, gum arabic, starch sugar and diabetic sugar, glycerine, and mannite. Tartaric, citric, malic, mucic, kinic, and pectic acids, produce the same effect. (ROSE. DUMAS.)

This oxide of iron is easily reduced by the action of hydrogen at a temperature even below redness. It consists of

				Bucholz.	Gay Lussac.	Strome- yer.	Ber- zelius.	Dobe- reiner.	Kla- proth.
Iron	1	28	70	70.423	70.27	69.85	69.22	69	67
Oxygen	1½	12	30	29.577	29.73	30.15	30.78	31	33
Peroxide of iron	1	40	100	100.000	100.00	100.00	100.00	100	100

BLACK OXIDE OF IRON. DEUTOXIDE OF IRON. FERROSO-FERRIC OXIDE. ($3fe + 4o$) or $(fe + o) + 2(fe + \frac{1}{2}o)$.—The octoëdral *magnetic iron ore* appears to be a definite compound of the two oxides as represented by the above formula. According to Gay Lussac a similarly constituted oxide is formed by passing the vapour of water over red-hot iron in a porcelain tube. (*Ann. de Chim.*, LXXX.; and *Ann. de Ch. et Ph.*, i.) The scales of iron obtained from the smith's forge, and the black powder formed by the action of air on moistened iron filings, and formerly called *Martial Ethiops*, are probably allied to this deutoxide, but in these the protoxide or peroxide may occasionally predominate, so that they can scarcely be regarded as definite in their composition. Liebig and Wöhler produced this oxide artificially by mixing dry protochloride of iron with excess of carbonate of soda, calcining the mixture in a crucible, and treating the mass with water. The double oxide remained as a black powder, capable of being washed and dried without change. "The same chemists, by dissolving the black oxide in hydrochloric acid, and precipitating by ammonia, obtained a hydrate of this oxide; it was attracted by a magnet even when a flocculent precipitate suspended in water. When ignited and anhydrous, this double oxide is much more magnetic than iron itself." (GRAHAM.) The composition of the true deutoxide, in reference to Gay Lussac's analysis, is

Iron	3	84	72.5
Oxygen	4	32	27.5
Deutoxide of iron	1	116	100.0

Native Oxides of Iron.—These constitute a very extensive and important class of metallic ores. They vary in colour, depending upon mere texture in some cases; in others, upon the degree of oxidizement. Some are magnetic, and those which contain least oxygen are attracted by the magnet. From them the commercial demands of iron are partly supplied: an outline of this manufacture will be given at the end of this Section, when the other combinations of the metal have been described. The following are some of the principal mineralogical varieties of the oxides of iron. (1.) *Magnetic iron ore* (*Fer oxidulé*) is generally black, with a slight metallic lustre. It occurs massive and octoëdral. It is often sufficiently magnetic to take up a needle; its specific gravity is 4.5. It occurs chiefly in primitive countries, and is very abundant at Roslagen in Sweden, where it is manufactured into a bar-iron particularly esteemed

for making steel. (2.) Another variety of native oxide of iron is called *iron-glance*, *specular*, and *micaceous iron-ore* (*Fer oligiste*). It is found crystallized of singular beauty, in the Isle of Elba; and occasionally among the volcanic products of Vesuvius and the Lipari Islands. (3.) *Hæmatite*, or red iron-stone: it occurs in globular and stalactitic masses, having a fibrous and diverging structure. In this country it abounds near Ulverstone in Lancashire; and much of our iron-plate and wire is made from it. Sometimes it is of a brown, black, or ochraceous colour. This, as well as the iron-glance, is a sesquioxide, and does not affect the magnet. There are also several varieties of *hydrated peroxide of iron*, such as the fibrous brown or black hæmatite, the lenticular and pisiform iron ore (*Fer limoneux*), and varieties of ochre and umber: these often degenerate into the next variety. (4.) A fourth variety of oxide of iron is known under the term of *clay-iron-stone*, on account of the quantity of argillaceous earth with which it is contaminated. It is found in masses of different shapes and sizes, and sometimes in small rounded nodules like peas. Some of the globular masses are called *ætites*. The iron-ore of the coal formations of Shropshire, South Wales, Staffordshire, and Scotland, (which, though far from the purest ore found in this country, is the principal source of the cast and bar iron, in ordinary use,) is chiefly a *carbonate*.

IRON AND CHLORINE unite in two proportions: forming a protochloride and a perchloride of iron, which in atomic composition are analogous to the oxides.

PROTOCHLORIDE OF IRON (*fe + c*) may be obtained, (1.) By passing dry hydrochloric acid gas over red-hot iron-wire or turnings; or (2.) By digesting clean iron-filings in hydrochloric acid, in which case, as in the former, hydrogen is set free; or by employing protosulphuret of iron instead of metallic iron, when sulphuretted hydrogen is evolved: in both cases a green solution is obtained which, evaporated out of the contact of air, leaves a residue which is to be exposed to a red heat. (3.) By heating a mixture of iron-filings and hydrochlorate of ammonia.

Protochloride of iron is of a dark-gray colour, and after fusion acquires a foliated crystalline texture; it is volatile at a high red-heat and may be condensed in pale-gray crystals; heated in air or oxygen it gives out chlorine, and leaves peroxide of iron. When the vapour of water is passed over it at a dull red-heat, hydrochloric acid and hydrogen are evolved, and black magnetic oxide of iron remains in the tube; exposed to damp air it evolves chlorine, and hydrochloric acid and peroxide of iron are also formed.

Protochloride of iron is soluble in water, furnishing a green solution, which soon changes by exposure to air, but which, evaporated in close vessels, yields tabular crystals, including 4 atoms of water: the solution absorbs nitrous gas and becomes of deep olive colour. This chloride is insoluble in absolute alcohol: it consists of

				J. Davy.
Iron	1	28	43·7	46·57
Chlorine	1	36	56·3	53·43
Protochloride of iron	1	64	100·0	100·00

PERCHLORIDE OF IRON. SESQUICHLORIDE OF IRON. ($fe + \frac{1}{2}c$) or ($2fe + 3c$).—When fine iron-wire is heated in excess of chlorine it burns with a red light, and this compound is formed: it is volatile at a heat below redness, and condenses in the form of brilliant and iridescent brown scales; it is very deliquescent and rapidly soluble in water, with the evolution of heat; when this solution is evaporated to dryness hydrochloric acid ultimately passes off, and peroxide of iron remains. The solution of this perchloride is easily obtained by dissolving peroxide of iron in hydrochloric acid; it forms a deep-brown liquid, which, when concentrated to the consistence of a syrup nearly, and then exposed to cold, yields crystals, the form of which varies, according to Mitscherlich, with their respective quantities of water: when they form acicular and radiating tufts they include 12 atoms of water, but when they form larger prisms, only 5 atoms. By exposing a solution of the protochloride to air, it passes into the brown perchloride; and according to Berzelius, if a dilute solution of the former be exposed for some days to the atmosphere in a tall jar, and a few drops of ammonia be then introduced at different depths, by means of a glass tube, the precipitate near the surface will be green; a little lower, blue; still lower, gray; then of a dirty white; and, at the bottom, quite white; provided the solution has not been so long exposed as to have become oxidized throughout. By saturating a strong solution of chloride of iron with chlorine, Van Mons obtained a brown liquid, which did not give out the odour of chlorine, and tasted astringent, slightly acid, and sweet: after a time, yellow crystals formed in it, and chlorine was evolved: the crystals soon deliquesced, and could not be obtained a second time. The protochloride and perchloride of iron perform the respective parts of base and of acid, in certain combinations. The perchloride is soluble in alcohol and in ether; the former solution is the *Tinctura ferri sesquichloridi* of the Pharmacopœia; and when ether is agitated with a solution of the perchloride it acquires a yellow colour. Perchloride of iron and peroxide of iron appear to form a definite compound. Perchloride of iron consists of

					J. Davy.				
Iron	1	28	34.1	35.1		
Chlorine	$1\frac{1}{2}$	54	65.9	64.9		
<hr/>					<hr/>				
Perchloride of iron	1		82		100.0		100.0		

AMMONIO-CHLORIDE OF IRON.—When hydrochlorate of ammonia and peroxide of iron are mixed and exposed to heat in a proper subliming vessel, a yellow sublimate is obtained, which is the *ens veneris*, *flores martiales*, and *ferrum ammoniatum* of old pharmacy; the *Ferri ammonio-chloridum* of the present Pharmacopœia. When a mixed solution of hydrochlorate of ammonia and perchloride of iron is set aside to crystallize, or evaporated in vacuo, it furnishes ruby-coloured cubic crystals, consisting of 2 equivalents of hydrochlorate of ammonia (chloride of ammonium), 1 of perchloride of iron, and 2 of water. Of this water, the double salt loses 1 equivalent at 150° , and the other, when dried above 300° .

POTASSIO-CHLORIDE OF IRON.—A double salt formed by mixing equivalent proportionals of chloride of potassium and perchloride of iron.

THE CHLORATES OF IRON have not been satisfactorily examined.

PROTIODIDE OF IRON ($fe + i$) is formed by digesting iron turnings or wire with iodine in water, taking care to have excess of metal present: a green solution is obtained, which, by evaporation out of contact of air, leaves a gray fusible protiodide of iron. It is soluble in water and alcohol, and the solution rapidly absorbs oxygen, and deposits peroxide of iron, unless metallic iron be present; so that to preserve it unchanged some pieces of clean iron-wire should be immersed in it. This solution has been advantageously employed in medicine by Dr. A. T. Thomson. By careful evaporation in vacuo crystals of a hydrated protiodide of iron, including 5 atoms of water, may be obtained from it. Protiodide of iron contains

Iron	1	28	18.2
Iodine	1	126	81.8
<hr/>			
Protiodide of iron	1	154	100.0

PERIODIDE OF IRON has not been examined, or, at least, not satisfactorily described: according to Berzelius, the brown powder which falls on exposing the solution of the protiodide to air is a *hydrated subperiodide*. According to Mr. Squire it is merely peroxide of iron, and no periodide exists. Dumas says that we obtain a solution of periodide of iron by dissolving hydrated peroxide of iron in hydriodic acid, and that a compound of periodide and peroxide of iron is thrown down when a quantity of potassa is added to a solution of the periodide, insufficient for its total decomposition; a yellow-brown powder then falls, which is an iodide of the oxide.

IODATE OF IRON.—Iodate of potassa throws down a yellowish precipitate in solution of protosulphate of iron, and a white precipitate in solution of perchloride of iron. (PLEISCHL.)

PROTOBROMIDE OF IRON.—When bromine vapour is passed over red-hot iron-wire, a yellow crystalline fusible bromide is obtained, readily soluble in water. (*Ann. de Ch. et Ph.*, xxxiii. 331.) At common temperatures bromine and iron act but feebly on each other; but if iron-filings, bromine, and water, be heated together, a solution of protobromide of iron is soon obtained. There appears to be the same uncertainty respecting the perbromide as belongs to the periodide of iron. The components of protobromide of iron are

Iron	1	28	26.43
Bromine	1	78	73.57
<hr/>			
Protobromide of iron	1	106	100.00

FLUORIDES OF IRON.—When iron is digested in hydrofluoric acid, a solution is obtained, which affords small quadrangular tabular crystals; they are colourless, and difficultly soluble in water. Heated rapidly in the air, this salt is decomposed; but if its water of crystallization be slowly and carefully expelled, it then may be fused into a true *fluoride of iron*. When hydrated peroxide of iron is dissolved in hydrofluoric acid, it forms a colourless solution, which yields flesh-coloured crystals, slowly soluble in water. Ammonia throws down a yellow precipitate, which is

a subfluoride: a double *fluoride of potassium and iron* is obtained in colourless crystals, when a mixed solution of those fluorides is evaporated. (BERZELIUS.)

NITRURET OF IRON. (*Azoture de fer.*)—It is stated by Dumas, on the authority of Desprets, that when ammonia is passed over ignited iron-wire, the whole of the hydrogen and much of the nitrogen of the ammonia are disengaged, but that a portion of the nitrogen is retained in permanent combination with the iron, varying from 6 or 7 to 10 or 11 per cent. The resulting compound is white, brittle, and even friable, magnetic, and less acted on by air and water than iron: it is specifically lighter than iron, its density being about 5. When strongly heated it loses its nitrogen, but the iron retains the appearance of the compound: the acids act upon it as upon iron, but disengage a mixture of hydrogen and nitrogen; besides which, ammonia is formed, which remains in combination with the acid.

PROTONITRATE OF IRON.—When very dilute nitric acid (specific gravity 1.16) is digested upon iron-filings, little gas is evolved, and the liquid assumes an olive-brown colour from the nitric oxide which it contains, but exposed to the air it becomes pale-green in consequence of the escape of that gas; the alkalis produce a green precipitate in this solution: it cannot be obtained in crystals by the usual process, and passes into pernitrates by exposure to air. It may, however, according to Thomson, be crystallized by evaporation in an exhausted receiver over sulphuric acid; it then forms transparent rhomboidal crystals of a light-green colour, composed of 1 atom of protoxide of iron, 1 of nitric acid, and 7 of water. When protosulphuret of iron is dissolved in dilute nitric acid sulphuretted hydrogen escapes, and a green solution of protonitrate of iron is obtained, which, when gently heated, speedily becomes brown, in consequence of the formation of peroxide. A protonitrate of iron is also formed when solutions of protosulphate of iron and nitrate of baryta are mixed in atomic proportions. The solution of the neutral protonitrate is decomposed near the boiling temperature with the evolution of nitric oxide, and the precipitation of a subnitrate of the peroxide, in abundance. Iron turnings dissolve in pure nitric acid, and form the same salt without the evolution of any gas, the water and acid undergoing decomposition so as to produce ammonia while they oxidate the iron. (GRAHAM.)

PERNITRATE OF IRON.—Nitric acid, diluted with a very little water, acts violently on iron and peroxidizes it, a vast quantity of gas being at the same time generated, which consists of a mixture of nitrous and nitric oxides; and a solution is formed of a reddish-brown colour, containing *pernitrate* of iron, and affording a brown precipitate to the alkalis. When evaporated, a brown deliquescent mass remains, soluble in water and alcohol. It is decomposed at a red heat, and peroxide of iron remains. If this solution be mixed with excess of carbonate of potassa, the precipitate at first thrown down is redissolved by the alkali, and a deep-brown liquid obtained, called in our *Pharmacopœia*, *Liquor ferri alkalini*; it has long been known in Germany under the name of "Stahl's alkaline tincture of iron." A crystallized pernitrates was obtained

by Vauquelin from a solution formed by leaving nitric acid long in contact of black oxide of iron: the crystals, which were square prisms and colourless, deliquesced into a reddish-brown liquid; they consist, according to Thomson, of 1 atom of peroxide of iron, $1\frac{1}{2}$ of nitric acid, and 8 of water.

Passive condition of Iron, in respect to the action of Nitric Acid.—In all ordinary cases nitric acid of the specific gravity of 1.35 acts powerfully upon iron, but under certain circumstances it becomes inert, and may be thrown, as it were, into a passive condition: a circumstance first noticed by Schoenbein. This state of things is brought about either by, 1. Slightly oxidizing the extremity of an iron-wire by holding it in the flame of a spirit lamp, and when cold dipping it gradually into the acid, observing to introduce the oxidized end first. 2. By dipping the end of the wire into strong nitric acid and washing it in water. 3. By first introducing a platinum wire into the acid, and then the iron-wire in contact with it, which contact may, however, afterwards be broken. 4. An iron wire already rendered passive acts as the platinum wire, and this renders other wires passive in the same way. 5. By making the iron wire the anelectrode or positive conductor of a voltaic pile, and introducing it into the acid after the insertion of the cathelectrode or negative pole: in this case the iron wire behaves as one of platinum, and gives off oxygen gas. This state is destroyed when the passive iron is made the negative pole, or when it is brought into contact with iron or zinc which at the time is in the act of solution by the acid. This condition of iron, connected apparently with its relations to magnetism or electricity, is not confined to nitric acid, but extends to other agents. (SCHOENBEIN and FARADAY, *Phil. Mag. and Ann.*, vols. ix. and xiv.)

PROTOSULPHURET OF IRON. (*fe + s.*)—1. When sulphur is dropped upon red-hot iron wire, or fused with iron-filings, a compound is obtained, which, after having been heated to expel excess of sulphur, is perfectly soluble in dilute sulphuric acid, with the evolution of pure sulphuretted hydrogen, and which is a protosulphuret of iron. 2. White-hot iron, exposed to a jet of sulphur vapour, burns in it, and runs down into the protosulphuret. 3. It is formed by exposing pure yellow pyrites, or bisulphuret of iron, intimately mixed with an equivalent of pure iron, to a red heat; or, 4, By passing dry hydrogen gas over powdered iron pyrites, heated to redness in a glass or porcelain tube. 5. It is thrown down in a hydrated state on adding hydrosulphuret of ammonia to solution of protosulphate of iron. 6. By the mutual action of iron-filings and powdered sulphur made into a paste with water.

Protosulphuret of iron is of a dark-bronze colour, and influences the magnet. It is much more fusible than iron: when pure it is soluble without residue in dilute acids with the evolution of sulphuretted hydrogen, and the formation of a protosalt of iron. When heated in air or oxygen, sulphurous acid and oxide of iron are formed. Digested in strong nitric or nitrohydrochloric acid, a portion of sulphur is separated, the iron is peroxidized, and sulphuric acid is formed. When the hydrated sulphuret is exposed to air the iron becomes oxidized, and sulphur separates, and more or less sulphurous and sulphuric acids are often formed, with heat enough to produce inflammation. This sulphuret consists of

				Hatchett.	Berzelius.	Proust.
Iron	1	28	63.6	63.5	63	62.5
Sulphur	1	16	36.4	36.5	37	37.5
Protosulphuret of iron	1	44	100.0	100.0	100	100.0

BISULPHURET OF IRON ($fe + 2s$) is formed, according to Berzelius, when the protosulphuret is well mixed with half its weight of sulphur, and subjected to a high temperature, which, however, must be below redness: a bulky, dark-yellow metallic powder is the result, which is not attracted by the magnet, and insoluble in dilute sulphuric and hydrochloric acid. A similar compound is obtained by passing a current of sulphuretted hydrogen over peroxide of iron at a temperature just below redness. If natural crystals of black oxide of iron be subjected to this process, they are converted without change of form into the bisulphuret. When exposed to heat in close vessels it loses half its sulphur, and becomes protosulphuret. We have two interesting cases of the formation of this sulphuret in the humid way. The one, described by Mr. Hatchett as occurring in the Mere of Diss, in Norfolk (*Phil. Trans.*, 1797); the other, by Mr. Pepys, in the *Geological Transactions*, vol. i., p. 399, and taking place in the bones of mice which had fallen into a solution of sulphate of iron. Bisulphuret of iron consists of

				Berzelius.	Hatchett.	Bucholz.
Iron	1	28	46.7	46.08	46.7	49
Sulphur	2	32	53.3	53.92	53.3	51
Bisulphuret of iron	1	60	100.0	100.00	100.0	100

Native Sulphurets of Iron.—Mr. Hatchett's experiments, above quoted, show that the ore of iron, called *magnetic pyrites*, is a protosulphuret of iron, and that *common pyrites* is a bisulphuret; the results of his analysis of these ores are given in the preceding paragraphs. Common pyrites is found, massive and crystallized, in a variety of forms, derived from a primitive cube; it often occurs in radiated nodules, which, when rolled amongst the shingles upon the sea-beach, are sometimes erroneously supposed to be of meteoric origin, and are called *thunder-bolts*. This mineral is of different shades of brass-yellow. The principal use of pyrites is in the formation of *sulphate of iron*, or *green vitriol*, for which purpose the ore is gently roasted and exposed to air and moisture. Some varieties are spontaneously decomposed, and furnish this salt, and when in large masses generate heat enough to become ignited: in this way beds of coal have been set on fire in consequence of the absorption of oxygen by their contained pyrites. Pyrites has also been used as a source of sulphur, and as a substitute for sulphur, in the production of sulphuric acid.

SESQUISULPHURET OF IRON. ($fe + \frac{1}{2}s$).—This compound is formed by passing sulphuretted hydrogen over peroxide of iron at a temperature not exceeding 212° ; or by the action of the same gas upon the hydrated peroxide at common temperatures. According to Proust, it may be formed by the action of sulphur on the protosulphuret at a very low red heat: he states it to be magnetic, which Berzelius denies. It is formed in the humid way by adding neutral persulphate of iron, drop by drop, to

a solution of an alkaline hydrosulphuret; it then falls as a black powder, which cannot be dried in the air without change. It corresponds in composition with the peroxide, and consists of

				Berzelius.	Proust.	Bucholz.
Iron	1	28	53.8	52.92	52.64	52.07
Sulphur	$1\frac{1}{2}$	24	46.2	47.08	47.36	47.93
Sesquisulphuret of iron	1	52	100.0	100.00	100.00	100.00

DISULPHURET OF IRON ($2fe + s$) is formed, according to Arfwedson, by passing a current of hydrogen gas over anhydrous protosulphate of iron, heated to redness: sulphurous acid, water, and sulphuretted hydrogen, are evolved, and 46.47 per cent. of the above compound remain. This is probably a definite compound of 1 atom of iron + 1 atom of protosulphuret of iron.

TETRA-SULPHURET OF IRON ($4fe + s$) is also described by Arfwedson as a definite sulphuret; he obtained it by passing a current of hydrogen over anhydrous subpersulphate (disulphate of the peroxide) of iron. These compounds are gray and pulverulent, and they both evolve mixtures of hydrogen and sulphuretted hydrogen when dissolved in dilute sulphuric acid.

HYPOSULPHITE OF PROTOXIDE OF IRON ($Fe + \underline{s}$) is obtained by digesting finely-divided metallic iron in sulphurous acid; a solution is obtained at first brown, but becoming green, and no gas is evolved: it does not crystallize, and when evaporated leaves a dirty-white viscid mass, and is decomposed by exposure to air. When sulphuric or hydrochloric acid are added to its solution, sulphurous acid is evolved, and sulphur precipitated. The solution of this hyposulphite furnishes one of the best instances of a pure protosalt of iron; and by keeping a few filings of iron in it, it may be retained in this state. It gives a perfectly-white precipitate with the ferrocyanuret of potassium, if dilute, and infusion of galls does not immediately discolour it.

PROTOSULPHITE OF IRON ($Fe + \underline{s}$) has not been accurately examined. It may be obtained by digesting recently precipitated protocarbonate of iron in an aqueous solution of sulphurous acid: a brown solution is obtained, from which, when concentrated, alcohol throws down the sulphite.

HYPOSULPHATE OF PROTOXIDE OF IRON is formed by mixing a solution of hyposulphate of baryta with protosulphate of iron: the filtered solution furnishes green prismatic crystals, easily soluble, and containing 29.54 per cent. of water of crystallization.

SULPHATES OF IRON.—Sulphuric acid forms salts with both the oxides of iron, and we have accordingly a *protosulphate*, and a *persulphate* of iron: the latter is sometimes incorrectly termed a *sesquisulphate*, because 1 proportional of peroxide of iron combines with $1\frac{1}{2}$ of sulphuric acid; but as the peroxide of iron contains 1 atom of iron united to $1\frac{1}{2}$ of oxygen, the acid of the salt is the proper equivalent to that of the oxygen in the oxide.

PROTOSULPHATE OF IRON is the *copperas* and *green vitriol* of commerce, and is often prepared by exposing roasted *pyrites* or *bisulphuret of iron* to air and moisture, in which case the salt is impure. It is usually formed for medicinal and chemical purposes, by dissolving iron-filings or turnings in dilute sulphuric acid, filtering and evaporating the solution, and setting it aside to crystallize. It is also obtained, perfectly free from persulphate, by acting upon the artificial *protosulphuret* of iron by dilute sulphuric acid. This salt forms, when pure, bluish-green crystals in the form of oblique rhombic prisms, (BROOKE, *Ann. of Phil.*, 2nd series, vi. 120,) of a styptic taste, reddening vegetable blues; and including, according to Thomson, 7 proportionals of water. The specific gravity of the crystallized salt is 1.8; that of the anhydrous sulphate, 2.64. (DUMAS.) The solubility of 1 part of crystallized sulphate of iron at different temperatures is, according to Brandes and Firnhaber, as follows. (GMELIN.)

Temperature	50°	59°	75°	92°	115°	140°	183°	194°	212°
Water	1.64	1.43	0.87	0.66	0.44	0.38	0.37	0.27	0.30

The solution is pale-green, and absorbs nitric oxide gas, acquiring a deep-brown colour; it also absorbs chlorine, and hydrochloric acid is formed, and the iron becomes peroxidized; so that water is here decomposed. It is insoluble in alcohol and in sulphuric acid, both of which deprive the crystals of water, and precipitate the salt from its solutions in the form of a white powder.

Exposed to dry air this salt effloresces; in moist air it gradually absorbs oxygen, and is partly converted into a persulphate, becoming of a rusty or reddish colour, whence the French term *couperose* applied to it, corrupted into *copperas*. It may also be converted into persulphate by nitric acid. When heated, it fuses in its water of crystallization, and at 238° loses 6 equivalents of water, but retains 1 equivalent till heated above 535°; this may be driven off at a higher temperature, and at a red heat it evolves anhydrous sulphuric acid, peroxide of iron remaining in the vessel: by this process sulphuric acid used formerly to be prepared, and the residue was known under the name of *caput mortuum vitrioli* or *colcothar*. Hence, also, it is, that sulphate of iron is often used as a substitute for sulphuric acid, to separate weaker acids from their bases, at high temperatures. Anhydrous protosulphate of iron ($fe + o$) + ($s + 3 o$) consists of

				Berzelius	Wenzel.
Protoxide of iron	1	36	47.4	47.07	42.17
Sulphuric acid	1	40	52.6	52.93	57.83
Anhydrous protosulphate of iron	1	76	100.0	100.00	100.00

and the ordinary crystals are composed of

				Berzelius.	Thomson.	Mitscherlich
Anhydrous protosulphate of iron	1	76	54.7	54.6	55	56.08
Water	7	63	45.3	45.4	45	43.92
Crystallized protosulphate of iron	1	139	100.0	100.0	100	100.00

When a solution of protosulphate of iron is made to crystallize at a temperature of 176°, it forms right rhombic prisms which include 4 equivalents of water, and correspond with the sulphate of manganese; and

when an acid solution of sulphate of iron is boiled down, a saline crust forms in which the salt is combined with 3 equivalents of water; lastly, by dissolving the salt in sulphuric acid, crystals may be obtained with 2 equivalents of water. (MITSCHERLICH.)

Native Green Vitriol is frequently found associated with iron pyrites, being produced by its decomposition: it occurs in several of our coal-mines. When exposed to air it suffers the same changes as the artificial salt. A *native persulphate of iron* occurs in white granular masses in Chili, forming beds in some places 20 feet deep. (ROSE, *POGGEND. Ann.*, xxvii.)

PROTOSULPHATE OF IRON AND AMMONIA is a triple salt, the crystals of which contain 8 proportionals of water, and are isomorphous with the ammonia-sulphate of magnesia. (MITSCHERLICH.)

PROTOSULPHATE OF IRON AND POTASSA is obtained by mixing solutions of proportionals of each of the salts; it is of a very pale tint of green, and the crystals contain 6 proportionals of water (MITSCHERLICH), 5 (THOMSON.)

PERSULPHATE OF IRON ($fe + \frac{1}{2}O + \frac{1}{2}S'$) is obtained by dissolving the moist red oxide in sulphuric acid; or by adding sulphuric acid to a solution of the protosulphate, heating the mixture, and dropping into it nitric acid sufficient to peroxidize the salt. It does not crystallize, but affords, by evaporation, a brown deliquescent mass. It is formed in the mother-waters of the sulphate. Its taste is highly astringent; it is soluble in alcohol; when dry it becomes white. When concentrated sulphuric acid is dropped into a strong solution of this persulphate, it throws it down in the form of a white anhydrous powder. This occasionally occurs in sulphuric acid of commerce, and has been mistaken for sulphate of lead. Persulphate of iron consists of

Peroxide of iron	1	40
Sulphuric acid	$\frac{1}{2}$	60
Persulphate of iron	1	100

According to Dumas, the protosulphate and persulphate of iron are capable of crystallizing together, and forming a kind of double salt; it is this which usually occurs under the name of green vitriol; it is of a dingy grass-green colour; whereas the pure sulphate of the protoxide furnishes hydrated crystals which are of a bright bluish-green.

SUBPERSULPHATE OF IRON.—When an aqueous solution of protosulphate of iron is exposed to air, or when a small addition of ammonia is made to the persulphate, a brown powder falls, composed, according to Berzelius, of 4 atoms of peroxide of iron and 1 of sulphuric acid: it is, therefore, a *tetrasubpersulphate*.

AMMONIO-PERSULPHATE OF IRON may be obtained in octoëdral crystals, which are colourless, and not unlike alum, by evaporating a mixed solution of sulphate of ammonia and excess of persulphate of iron. This salt, according to Forchammer (*Ann. of Phil.*, v.), is composed of

					Forchhammer.	
Persulphate of iron	2	200	14.5	41.95		
Sulphate of ammonia	1	57	11.8	12.11		
Water	25	225	46.7	45.94		
Persulphate of iron and ammonia	1	482	100.0	100.00		

When ammonia is cautiously added to a solution of persulphate of iron, and the mixture left to spontaneous evaporation, six-sided prismatic crystals are deposited, composed, according to Maus (POGGEND., vol. xi. p. 79), of

Sulphuric acid	49.20
Ammonia	10.30
Peroxide of iron	23.75
Water	16.75
	100.00

PERSULPHATE OF IRON AND POTASSA forms octoëdral crystals much resembling alum in form, colour, and taste. These crystals are occasionally found amongst those of common alum, and are a most inconvenient impurity. They are decomposed by repeated solution in water: they consist, according to Mitscherlich, of

Persulphate of iron	2	200	39.0
Sulphate of potassa	1	88	17.1
Water	25	225	43.9
Persulphate of iron and potassa	1	513	100.0

PHOSPHURET OF IRON. DIPHOSPHURET OF IRON ($2fe+p$) may be formed by dropping phosphorus into a crucible containing red-hot iron-wire; it is a brittle gray compound, and sometimes crystallizes in rhomboidal prisms. It acts upon the magnet. (Upon the subject of the magnetic qualities of the sulphuret and phosphuret of iron, the reader is referred to Mr. Hatchett's analysis of the magnetical pyrites. *Phil. Trans.*, 1804.) It may also be procured by the ignition of a mixture of iron-filings, phosphoric acid, and charcoal powder; or by decomposing phosphate of iron by charcoal. It is very difficultly soluble in the acids. A small portion of this compound is said to be present in all *cold-short iron*, and is eminently injurious to the quality of iron when it is contained in it to the amount of 1 per cent. Steel which does not contain more than 1 part in 1000 of phosphuret of iron is rendered harder, and for some particular purposes improved.

Phosphuret of iron obtained by the above processes, consists of

					Berzelius.	Pelletier.
Iron	2	56	77.8	76.805	80	
Phosphorus	1	16	22.2	23.195	20	
Phosphuret of iron	1	72	100.0	100.000	100	

When phosphuretted hydrogen gas is passed over heated iron pyrites, a compound is formed, containing 54.92 to 56.87 iron + 45.08 to 43.13 phosphorus. (H. ROSE.) No definite compound of phosphorus and iron in single atomic proportions has been obtained; the diphosphuret combines readily by fusion in all proportions with iron; but where a larger proportion of phosphorus is added, it burns away, and is never retained in greater quantity than about 22 per cent.

PROTOPHOSPHATE OF IRON ($\text{Fe} + p'$) is insoluble, and may be formed by adding solution of phosphate of soda to protosulphate of iron. The *protophosphate* of iron is at first white, but soon becomes blue by exposure; it is soluble in most of the acids, from which it may again be precipitated by ammonia. When it has acquired a full blue tint, it is probably analogous to the native phosphate, and is a hydrated compound of the phosphate of the protoxide with subphosphate of the peroxide.

PERPHOSPHATE OF IRON is a white insoluble precipitate, formed by adding phosphate of soda to persulphate or perchloride of iron: when heated it gives out water and becomes brown. Digested with potassa or soda it is converted into a brown *subperphosphate*.

These phosphates have been analyzed by Vogel (*Ann. of Phil.*, xiii. 310), and although some of his results might be represented by formulæ, others are apparently inconsistent with the usually accepted equivalents.

Native Phosphate of Iron occurs in the form of a blue earthy powder; or if at first white, it becomes blue by exposure: it also is found in prismatic crystals. The former has sometimes improperly been termed *Native Prussian Blue*, and has been found in alluvial soil: the latter occurs with iron pyrites in Cornwall. The blue crystallized variety analyzed by Stromeyer (*Untersuchungen*, i. 274), afforded

Phosphoric acid	31
Protoxide of iron	41
Water	28

100

IRON AND CARBON. CARBURET OF IRON.—It is doubtful how far any true atomic compound of iron and carbon can be obtained. I have already adverted to the claims of *graphite* to be so considered, and in a subsequent paragraph the composition of *cast-iron*, in reference to the carbon it contains, will be noticed. It has been observed by Berzelius, that some of the combinations of oxide of iron with organic acids may possibly yield by calcination definite carburets; the residues of the calcination of Prussian blue, and of ferrocyanuret of ammonium, are also combinations of iron and carbon, but how far these contain also nitrogen is a question which has not been adequately examined. By long continued fusion of steel with charcoal, Stodart and Faraday obtained a highly crystalline compound containing between 5 and 6 per cent. of carbon, and apparently therefore definite in its nature. All these compounds are principally interesting in reference to their influence upon the properties of cast-iron and steel, under which they will again be recurred to.

Considerable difficulty attends the analysis of compounds of carbon and iron, in estimating the proportion of the former; this has generally been indirectly effected by ascertaining the quantity of iron, and considering the loss of weight as carbon; a method obviously objectionable. If the action of dilute sulphuric acid be resorted to, a portion of carbon is carried off by hydrogen; the same is the case with hydrochloric acid; and if nitric acid be used, some carbonic acid may be formed, and artificial tannin is produced. Perhaps the best method is to mix 5 grains of the compound (such as cast-iron or steel) reduced to powder or fine filings

with 60 or 80 grains of chromate of lead; about a fourth part of this mixture is then put aside, and 5 grains of chlorate of potash are added to and well mixed with the remainder; this treble mixture is then put into a tube similar to those used in organic analyses, and the portion of the mixture without the chlorate is afterwards put upon it; the tube is then properly adapted to Liebig's apparatus. The portion of the tube is then heated which contains the mixture without the chlorate, and when this is red hot, the heat is successively applied to the whole; in this way the carburet is burned by the oxygen of the chlorate, a very minute quantity only of oxygen escaping; the oxidizement is afterwards continued at the expense of the chromate. It is convenient to protect the tube by a strip of thick leaf copper folded round it in order to enable it to bear the temperature requisite for the fusion of the chromate of lead. In three experiments, 5 grains of the same cast-iron gave

0.582	carbonic acid	=	3.22	of carbon per cent.
0.585	"	=	3.23	"
0.588	"	=	3.25	"

(REGNAULT, *Ann. de Ch. et Ph.*, LXX. 107.)

PROTOCOLCARBONATE OF IRON. ($\text{Fe} + \text{CAR}^{\text{I}}$).—Carbonic acid may be combined with the protoxide of iron, by adding carbonate of potassa to solution of protosulphate of iron; a white or greenish precipitate of hydrated *protocarbonate of iron* falls, which, exposed to air, becomes brown and evolves carbonic acid; so that a dry protocarbonate of iron cannot thus be obtained. Solution of bicarbonate of potassa occasions a white precipitate with sulphate of iron, part of which is redissolved on adding excess of the carbonated alkali. When carbonic acid in aqueous solution is digested with iron-filings, a colourless solution of the protocarbonate is obtained: it is not an uncommon ingredient in mineral waters, where it is held in solution by excess of carbonic acid. It consists of

Protoxide of iron	1	36	62
Carbonic acid	1	22	38
Protocarbonate of iron	1	58	100

Native Protocarbonate of Iron, or *Spathose Iron Ore*, occurs in Germany, and in some parts of Cornwall, crystallized in imperfect rhomboids. Its primary form is a rhomboid closely resembling that of carbonate of lime. Its colour is yellowish, or brownish-gray. It generally contains manganese, lime, and a trace of magnesia. A specimen of this mineral from Eulenloh in Bareuth, analyzed by Bucholz (GEHLEN'S *Journ.*, i. 231), contained carbonic acid 36, protoxide of iron 59, lime 3, water 2. These components indicate that this mineral consists essentially of protocarbonate of iron, composed as above. The *clay iron ore* of our coal districts, from which British iron is chiefly obtained, is an impure *protocarbonate of iron*. Previous to reduction, it is reduced by heat to the state of oxide, as will appear from the account of the manufacture of iron, at the end of this section. The following table shows the composition of six specimens of the clay-ironstone from the coal-beds of the neighbourhood of Glasgow, analyzed by Dr. H. Colquhoun. (BREWSTER'S *Journ.*, vii. 234.)

Carbonic acid . . .	32.53	33.63	31.86	30.76	26.35	33.10
Protoxide of iron . .	35.22	45.84	42.15	38.80	36.47	47.33
Protoxide of manganese	—	0.20	—	0.07	0.17	0.13
Lime	8.62	1.90	4.93	5.30	1.97	2.00
Magnesia	5.10	5.90	4.80	6.70	2.70	2.20
Silica	9.56	7.83	9.73	10.87	19.20	6.63
Alumina	5.34	2.53	3.77	6.20	8.03	4.30
Peroxide of iron . .	1.16	—	0.80	0.33	0.40	0.33
Coaly matter . . .	2.13	1.86	2.33	1.87	2.10	1.70
Sulphur	0.62	—	—	0.16	—	0.22
Moisture	—	0.99	—	—	—	—
	100.37	100.68	100.37	101.00	98.09	97.94

PERCARBONATE OF IRON has not been obtained in a separate state; for the protocarbonate, whilst drying, exposed to air, loses carbonic acid, and becomes peroxide. When bicarbonated alkalis are digested with recently-precipitated peroxide of iron, triple salts are formed.

IRON AND CYANOGEN.—These substances give rise to several important compounds, in which they exist either combined in various proportions, or as a *basis*, in union with other bodies.

PROTOCYANURET OF IRON (*fe + cy*) is obtained, according to Berzelius, in the form of a gray powder, by gently heating ammonio-cyanuret of iron (Ferrocyanate of Ammonia) out of the contact of air. It is formed, according to Robiquet, by digesting recently-prepared Prussian blue in a well-stopped phial with a saturated solution of sulphuretted hydrogen; it becomes white, and the solution contains hydrocyanic acid. When solutions of cyanuret of potassium and protosulphate of iron are mixed, an abundant reddish precipitate falls, which is redissolved by excess of the cyanuret, and then forms ferrocyanuret of potassium. Upon the whole, it is doubtful whether a pure proto-cyanuret of iron has been isolated: its components are

Iron . . . 1 . . .	28 . . .	51.9	Iron . . .	51.9
Carbon . . . 2 . . .	12 . . .	22.2	Cyanogen	48.1
Nitrogen . . 1 . . .	14 . . .	25.9		
	1 . . .	54		
		100.0		100.0

According to Pelouze (*Ann. de Ch. et Ph.*, lxi. 40), a combination of cyanogen and iron, corresponding to the black magnetic or deutoxide of iron, is obtained by passing a current of chlorine into a boiling solution of ferrocyanuret of potassium; a green powder precipitates, which is to be boiled in 8 or 10 parts of concentrated hydrochloric acid, by which peroxide of iron and Prussian blue are dissolved, and a green powder remains, which, when washed and dried in vacuo, constitutes this intermediate combination. Heated to 355° it loses water, cyanogen, and a little hydrocyanic acid, and acquires a deep purple colour. In a solution of caustic potassa it is converted into peroxide of iron, and a mixture of the ferrocyanurets of potassium.

PERCYANURET OF IRON. SESQUICYANURET OF IRON. (*fe + 1½ cy*) or (*2 fe + 3 cy*).—This compound has not been isolated. It is obtained in solution when ferrosesquicyanuret of potassium is decomposed by fluoride of silicon, forming a brown astringent liquid; but on evaporation it deposits Prussian blue. (See *Ferrosesquicyanurets*.)

FERROCYANURETS.—Protocyanuret of iron, which we may call *ferrocyanogen*, combines with a variety of other metallic cyanurets, forming double cyanurets, or *ferrocyanurets*, and they are generally so constituted as to contain 1 equivalent of the ferrocyanogen combined with 2 equivalents of the other cyanuret: their elements, therefore, are in such a ratio, that if the metals were converted into *protoxides* at the expense of water, the hydrogen would just suffice to form hydrocyanic acid with the cyanogen; or, in other words, *one* equivalent of the respective ferrocyanurets would decompose *three* equivalents of water.

[Liebig applies the term *ferrocyanogen* to a hypothetical compound (salt-radical) of 3 atoms of cyanogen and 1 of iron ($fe + 3cy$), and he designates by the term *ferricyanogen* (Ferridcyanogen of Turner) a salt-radical containing 6 atoms of cyanogen and 2 of iron ($2fe + 6cy$).]

The *ferrocyanurets* are decomposed by heat with various phenomena.

1. The ferrocyanogen evolves nitrogen and becomes converted into bicarburet of iron, which remains mixed with the basic cyanuret; this is the case with *ferrocyanuret of potassium*.
2. The cyanogen of both the cyanurets is decomposed, nitrogen evolved, and metallic bicarburets of iron and of the basic metal are formed, as with *ferrocyanuret of lead*.
3. The basic cyanuret evolves cyanogen, and is reduced, as in the case of *ferrocyanuret of silver*.

FERROCYANURET OF POTASSIUM. FERROCYANATE OF POTASSA. PRUSSIAN OF POTASSA. ($fe + cy$) + 2 ($po + cy$).—When *Prussian blue* is boiled with potassa it is decomposed; it loses its blue colour; oxide of iron is separated; and on filtering and evaporating the solution, crystals of the above compound are obtained. It is best formed by adding powdered Prussian blue (previously heated with a dilute sulphuric acid composed of 1 part of acid and 5 of water, and afterwards washed), to a hot solution of potassa, as long as its colour is destroyed. It is largely prepared as an article of commerce, chiefly for the use of calico-printers, by the following process:—

“Into an egg-shaped *iron* pot, brought to moderate ignition, project a mixture of good pearl-ash and dry animal matters, of which hoofs and horns are best, in the proportion of 2 parts of the former to 5 of the latter. Stir them well with a flat *iron* paddle. The mixture, as it calcines, will gradually assume a pasty form, during which transition it must be tossed about with much manual labour and dexterity. When the conversion into a chemical compound is seen to be completed by the cessation of the fetid animal vapours, remove the pasty mass with an iron ladle. If this be thrown, while hot, into water, some of the prussic acid will be converted into ammonia, and of course the usual product diminished. Allow it to cool, dissolve it in water, clarify the solution by filtration or subsidence, evaporate, and, on cooling, yellow crystals of the ferroprussiate of potash will form. Separate these, redissolve them in hot water, and, by allowing the solution to cool very slowly, larger and very regular crystals may be had.” (URE’S *Dictionary*.)

Mr. Charles Macintosh, of Glasgow, who is one of the largest manufacturers of this salt, informs me that the animal matters employed as the source of cyanogen are chiefly chips of horns, animal hoofs, woollen rags,

and the substance called *greaves*, which is the refuse of tallow-melters, and consists chiefly of cellular membrane from which the fat has been expressed: these are burned, and, in fact, fused at a very high heat with potash, to form what is called *prussiate cake*; this, when cold, is lixiviated with water, and the evaporated solution yields a first crop of very impure ferroprussiate; it is redissolved, and the second crystallization is allowed to go on very slowly, it being at least a fortnight before the contents of the coolers are disturbed. The iron requisite to the constitution of this salt is derived from the iron pots and stirrers used in the operation, or, if requisite, iron filings are added.

The following explanation of the theory of this process is from Liebig. When animal substances containing carbon and nitrogen are fused with potash at a red heat, the potassium is reduced by the carbon, and forms by its reaction on the other ingredients cyanuret of potassium. The fused mass at a red heat contains no ferrocyanogen, but iron and carburet of iron in the form of a suspended powder. When it is lixiviated with cold water and immediately evaporated, it furnishes no ferrocyanuret; but when the solution is gently heated for several hours in the contact of air, oxygen is absorbed, it acquires a yellow colour, and now contains much ferrocyanuret of potassium. This explains why a solution of cyanuret of potassium in pure water and in the presence of finely-divided metallic iron, absorbs the oxygen of the air in passing into the state of oxide of potassium and dissolving the metal; the potassium of the cyanuret, in yielding to the iron the cyanogen with which it was combined and so forming cyanuret of iron, enables it to combine with the remaining undecomposed cyanuret of potassium to form ferrocyanuret of potassium. In close vessels the solution of iron by cyanuret of potassium evolves hydrogen. The fused mass also contains free potassa, which, by being boiled with the cyanuret of potassium, decomposes it into formiate of potassa and ammonia. When animal substances are fused in open vessels with potassa, cyanate of potassa is formed, which is decomposed by boiling into ammonia and bicarbonate of potassa; the quantity of ammonia formed being in proportion to the loss of cyanuret of potassium.

The best way of converting the whole of the cyanuret into ferrocyanuret of potassium, is to treat one-third of a cold solution of the raw mass with protosulphate of iron, as long as a precipitate falls, and then to add the remaining two-thirds of the solution, and heat the whole to the boiling-point; the solution may then be evaporated without decomposition, and the sulphate of potassa is easily separated by crystallization from the ferrocyanuret. The original solution of the fused mass generally contains sulphuret and sulphocyanuret of potassium, and formiate and carbonate of potassa, which remain in the mother liquor.

Mr. L. Thompson has observed that cyanuret of potassium is abundantly formed when an ignited mixture of coke or charcoal, carbonate of potassa, and iron-filings, is exposed to the action of the air. In that process he says the potassa is decomposed by the iron, and that the evolved potassium combines with the carbon, and also with the nitrogen of the atmosphere; and that the cyanuret of potassium results from this action. He proposes to apply this process to the manufacture of Prussian blue. (*Trans. Soc. Arts*, lii. 24.)

Ferrocyanuret of potassium forms permanent lemon-yellow crystals, of a specific gravity of 1.83: they are insoluble in alcohol, which throws down the salt in yellow flakes from its aqueous solution. Water at 60° takes up about one-third, and at 212°, its own weight of this salt. (URE.) According to others it is soluble in 4 of cold and 2 of boiling water. It has a bitter, saline, and sweetish taste, and is not poisonous. The large crystals are tough, and the thin ones somewhat elastic: their forms have been described by Levy and Brooke. (*Quart. Journ.*, xv. 288; *Ann. of Phil.*, N. S., vi. 41.) They are four-sided tables, derived from a primary octoëdron. When moderately heated this salt loses its colour, and crumbles into powder, parting with about 13 per cent. of water. The crystals retain their figure till upon the verge of ignition. By a red heat it is converted with the escape of nitrogen into carburet of iron and cyanuret of potassium: when exposed to air the latter salt becomes cyanate of potassa. Boiled with dilute sulphuric or hydrochloric acids, hydrocyanic acid is given out, and a white precipitate formed similar to that which the salt produces in a solution of protosulphate of iron. By nitric acid and by chlorine it is converted into ferrosesquicyanuret of potassium.

Neither sulphuretted hydrogen, the hydrosulphurets, the alkalis, nor tincture of galls, produce any precipitate in solutions of this salt. Red oxide of mercury decomposes it at a moderate heat, peroxide of iron and metallic mercury are precipitated, and *cyanuret of mercury* formed; so that the iron is peroxidized at the expense of the oxide of mercury.

When a solution of this salt forms insoluble precipitates in metallic solutions, the nature of the metal present may often be judged of by the character and colour of the precipitate, as indicated by the following table:—

MANGANESE	Neutral protochloride	White
IRON . . .	Neutral protosulphate	White or pale blue
Ditto . . .	Perchloride	Prussian blue
ZINC . . .	Chloride	Yellowish white
TIN . . .	Acid protochloride	White, then yellow and bluish
Ditto . . .	Acid perchloride	Pale yellow,
CADMIUM .	Chloride	White
COPPER . .	Protochloride	Lilac
Ditto . .	Pernitrate	Deep brown
LEAD . . .	Nitrate	White
ANTIMONY .	Tartrate of antimony and potassa	0
BISMUTH .	Tartrate of bismuth and potassa	0
COBALT . .	Chloride	Pale green
URANIUM .	Sulphate	Deep brown
TITANIUM .	Acid chloride	Deep blue (from acid)
Ditto . .	Neutral sulphate	Sap green
ARSENIC .	White oxide	
Ditto . .	Arsenic acid	
NICKEL . .	Sulphate	Gray
MERCURY .	Acid nitrate	Greenish white
Ditto . .	Acid pernitrates	Ditto
Ditto . .	Corrosive sublimate	White
PALLADIUM	Chloride	Olive
SILVER . .	Nitrate	Cream-colour
GOLD . . .	Chloride	0
PLATINUM .	Chloride	Yellow

Various opinions have been entertained with regard to the proximate composition of the salt we have been describing. In its crystalline form it is, according to Berzelius, a *hydrated ferrocyanuret of potassium*, and I have adopted this as the simplest view of its constitution; that is, as consisting, in its *anhydrous* state, of 1 atom of cyanuret of iron, combined with 2 atoms of cyanuret of potassium. In this state, therefore, its ultimate elements are

						Robiquet.
Iron	. .	1	. .	28	. .	15 . . 14.9
Potassium	2	. .	80	. .	43	. . 42.9
Cyanogen	3	. .	78	. .	42	. . 42.2
	<u>1</u>		<u>186</u>		<u>100</u>	<u>100.0</u>

These elements are equivalent to

Cyanuret of iron	. .	1	. .	54	. .	29
Cyanuret of potassium	2	. .	132	. .	71	
	<u>1</u>		<u>186</u>		<u>100</u>	

And the *hydrated* or *crystallized ferrocyanuret*, will consist of

						Ure. Döbereiner.
Anhydrous ferrocyanuret of potassium	1	. .	186	. .	87.3	. . 88
Water	3	. .	27	. .	12.7	. . 12.88
	<u>1</u>		<u>213</u>		<u>100.0</u>	<u>100.00</u>

According to Liebig ferrocyanuret of potassium contains 1 equivalent of the salt-radical above adverted to (composed of 1 equivalent of iron and 3 of cyanogen), combined with 2 of potassium (*fe + 3 cy*) + (*2 po*), which again gives the equivalent 186 for the anhydrous salt.

Another view of the constitution of the hydrated salt has been founded upon the experiments of Porrett (*Phil. Trans.*, 1814). It will be observed that 1 atom of the anhydrous ferrocyanuret is combined with *three* atoms of *water*, the *oxygen* of which is obviously just that required to convert the iron and the potassium into protoxides, and the *hydrogen* to convert the cyanogen into hydrocyanic acid; so that, viewed in this way, the salt has been regarded as composed of

Hydrocyanate of protoxide of iron	. .	1	. .	63	. .	29.6
" of potassa	2	. .	150	. .	70.4
Crystals of ferrocyanuret of potassium		<u>1</u>		<u>213</u>		<u>100.0</u>

But Mr. Porrett conceived the protoxide of iron to be so combined with the whole of the hydrocyanic acid, as to constitute a distinct acid, which he termed ferruretted cyanic, or *ferrochyazic* acid (from the initial letters of carbon, hydrogen, and azote.)

BIFERROCYANURET OF POTASSIUM.—When a mixture of the preceding ferrocyanuret of potassium with sulphuric acid is subjected to distillation, hydrocyanic acid is evolved, and a ferrocyanuret, represented by the formula $2(fe + cy) + (po + cy)$, is among the products. Mr. Everitt has termed this ferrocyanuret "yellow salt," in the following diagram, showing the changes which ensue when 6 atoms of concentrated sulphuric acid are heated with 2 atoms of crystallized ferrocyanuret of potassium. (PHILLIPS, *Translation of London Pharmacopœia*.)

Before Distillation.			After Distillation.		
	Atoms.	Equivalents.		Atoms.	Equivalents.
Sulphuric acid	6	240	Bisulphate of potassa . .	3	384
Cyanuret of potassium . .	4	264	Hydrocyanic acid	3	81
Cyanuret of iron	2	108	Cyanuret of potassium . .	1	66
Water { 6 in the acid } . .	12	108	Cyanuret of iron	2	108
Water { 6 in the salt } . .			Water	9	81
		720			720

According to Gay Lussac, the result of the action of sulphuric acid upon ferrocyanuret of potassium is a *white* powder, which, after having been well washed with boiling water, and exposed to air, acquires a dingy blue tint, but becomes deep blue when moistened by dilute sulphuric acid, and yields sulphate of potassa: this *white ferrocyanuret* consists, he says, of 7 atoms of iron, 2 of potassium, and 9 of cyanogen: by the dilute acid, the 2 atoms of potassium are abstracted, and the remaining 7 of iron and 9 of cyanogen form Prussian blue. (*Ann. de Ch. et Ph.*, xlvi. 78.)

FERROCHYAZIC ACID. HYDROCYANOFERRIC ACID (of Gay Lussac).
 HYDROFERROCYANIC ACID. FERROCYANIC ACID. (*fe + o*) + ³(*cy + h.*)
 —This acid may be obtained, according to Porrett, as follows:—Dissolve 58 grains of crystallized tartaric acid in alcohol, and pour the solution into a phial containing 50 grains of ferrocyanuret of potassium, dissolved in 3 drachms of warm water; by these means the potassa is precipitated in the state of supertartrate, and the ferro-chyazic acid remains dissolved in the alcohol, from which it may be obtained, by careful evaporation, in small cubic crystals (*Ann. of Phil.*, Sept. 1818); or a solution of ferrocyanuret of barium may be decomposed by sulphuric acid, so as exactly to abstract the baryta in the form of sulphate. Berzelius recommends the decomposition of recently-precipitated ferrocyanuret of lead or copper diffused through water, by sulphuretted hydrogen, filtering, and getting rid of the excess of sulphuretted hydrogen, which would spoil the air-pump, by a little ferrocyanuret of lead: the solution should ultimately be rapidly filtered, and evaporated in vacuo over sulphuric acid. A white residue remains, which, when dissolved in water, is sour, inodorous, and yields Prussian blue with a persalt of iron; it dissolves the alkaline carbonates with effervescence, and yields *ferrocyanurets*. Its aqueous solution, when exposed to light and air, gradually deposits Prussian blue, and, when boiled, deposits white protohydrocyanate of iron. Subjected to destructive distillation it yields hydrocyanic acid, hydrocyanate, and carbonate of ammonia, and leaves carburet of iron. This acid consists, according to Berzelius (and Porrett?), of

Protoxide of iron	1	36	30.8
Hydrocyanic acid	3	81	69.2
Hydroferrocyanic acid	1	117	100.0

and the crystallized ferrocyanuret of potassium *may* be regarded as an anhydrous disalt of this acid, or as consisting of

Hydroferrocyanic acid	1	117	55
Potassa	2	96	45
Crystals of ferrocyanuret of potassium	1	213	100

According to Liebig the constituents of the hydroferrocyanic acid are $(3\text{cy} + \text{fe}) + 2\text{h}$, to which if we add 1 atom of water, we get the formula $(3\text{cy} + \text{fe}) + 2\text{h} + (\text{h} + \text{o})$, which are the elements of 1 atom of protoxide of iron and 3 of hydrocyanic acid, or $(\text{fe} + \text{o}) + 3(\text{cy} + \text{h})$.

FERROCYANURET OF AMMONIUM. FERROCYANATE OF AMMONIA.—When ferrocyanuret of lead is diffused through water, holding carbonate of ammonia in solution, or when Prussian blue is digested in solution of ammonia, the filtered liquors yield small yellow octoëdral crystals, which are transparent, permanent in the air, very soluble in water, and insoluble in alcohol. By boiling-water this salt is converted into cyanuret of ammonium and cyanuret of iron. When equal parts of ferrocyanuret of potassium and sal-ammoniac are boiled together in 6 parts of water, large brittle crystals of a lemon-yellow colour are deposited on cooling, composed, according to Bunsen, of 1 equivalent of ferrocyanuret of ammonium, 1 of sal-ammoniac, and 3 of water.

The constituents of the crystals of ferrocyanuret of ammonium appear to be

Iron	1	28	16·8
Ammonia	2	34	20·4
Cyanogen	3	78	46·6
Water	3	27	16·2
<hr/>			
Crystals of ferrocyanuret of ammonium	1	167	100·0

FERROCYANURET OF SODIUM. $(\text{fe} + \text{cy}) + 2(\text{so} + \text{cy})$.—This salt is obtained by boiling Prussian blue with caustic or carbonate of soda. Its solution yields hydrated yellow quadrangular prismatic crystals, soluble in 4·5 of water at 55°, and insoluble in alcohol. They effloresce, and lose by drying 40 per cent. of water. Their components are

Iron	1	28	10·7
Sodium	2	48	18·3
Cyanogen	3	78	29·8
Water	12	108	41·2
<hr/>			
Crystals of ferrocyanuret of sodium	1	262	100·0

FERROCYANURET OF BARIUM $(\text{fe} + \text{cy}) + 2(\text{ba} + \text{cy})$, is obtained by digesting Prussian blue in hot baryta water: as it cools, yellow rhomboidal prisms are deposited. The salt requires 100 parts of boiling water and 1920 of cold water for its solution. The crystals contain 18 per cent. or 6 equivalents of water, of which the greater part may be expelled at 212°.

FERROCYANURET OF STRONTIUM $(\text{fe} + \text{cy}) + 2(\text{str} + \text{cy})$ is formed by boiling a mixture of Prussian blue and hydrate of strontia in water: it forms yellow crystals soluble in 4 parts of cold water.

FERROCYANURET OF CALCIUM. $(\text{fe} + \text{cy}) + 2(\text{cal} + \text{cy})$.—When hydrate of lime and Prussian blue are boiled in water, and the resulting solution filtered and evaporated to the consistence of syrup, it yields large lemon-yellow four-sided prisms which effloresce in a warm atmosphere, and at 212° lose nearly 40 per cent. of water, retaining about 2 per cent. which cannot be separated except at a higher temperature.

FERROCYANURET OF MAGNESIUM crystallizes in small deliquescent tables.

FERROSESQUICYANURETS. FERRIDCYANURETS. FERRICYANURETS. — A *sesquicyanuret of iron*, or a compound of 1 atom of iron and $1\frac{1}{2}$ of cyanogen, ($2fe + 3cy$), cannot be obtained in an insulated state; but such a compound acts the same part as the *protocyanuret of iron* in regard to basic cyanurets, and produces a class of definite compounds which have been termed *ferrosesquicyanurets*. (L. GMELIN.) The compound which we have here termed *ferrosesquicyanogen*, Liebig designates *ferricyanogen*, which is translated by Turner into *ferridecyanogen*, the difference between *ferrocyanuret* and *ferricyanuret* not being adequately distinctive; but he takes a different view of the composition of this salt-radical, and represents it by the formula ($2fe + 6cy$) or $2(fe + 3cy)$.

FERROSESQUICYANURET, FERRICYANURET, or FERRIDCYANURET OF POTASSIUM.—When chlorine is passed through a solution of *ferrocyanuret of potassium* till it ceases to precipitate Prussian blue from the *persalts* of iron, and the fluid then filtered and slowly evaporated, it furnishes right rhombic prismatic crystals, which, purified by a second solution, assume a ruby-red colour; they are anhydrous, and require 3·8 parts of cold water for solution, and are nearly insoluble in alcohol. They burn with brilliant scintillations, and when heated in close vessels give off cyanogen and nitrogen, and leave *ferrocyanuret of potassium* and *carburet of iron*. When dissolved in water this salt is decomposed by sulphuretted hydrogen, sulphur and cyanuret of iron are precipitated, and hydrocyanic acid and *ferrocyanuret of potassium* formed. Although this salt occasions no change in solutions of iron containing the peroxide only, it is a most delicate test of the *protoxide* of that metal. This salt (doubling the equivalents, to avoid fractions) is constituted of

					L. Gmelin.
Iron	2 . . .	56 . .	16·9 . .	17·22	
Potassium	3 . . .	120 . .	36·1 . .	35·65	
Cyanogen	6 . . .	156 . .	47·0 . .	49·00	
	1	332	100·0	101·87	

Or, of

2 equivalents of sesquicyanuret of iron	$2(fe + 1\frac{1}{2}cy)$	$(67 \times 2) = 134$..	40·4
3 „ „ cyanuret of potassium	$3(po + cy)$	$(66 \times 3) = 198$..	59·6
		332		100·0

Or, according to Liebig,

1 equivalent of ferridecyanogen	$(2fe + 6cy)$	212	..	64
3 „ „ potassium	$(3po)$	120	..	36
		332		100

Although the action of chlorine furnishes the readiest mode of converting *ferrocyanuret* into *ferrosesquicyanuret of potassium*, there are other agents by which the same change may be effected. (SMEE, *Phil. Mag. and Ann.*, Sept. 1840.)

The *ferrosesquicyanurets of sodium, barium, and calcium*, may be obtained by the same process, care being taken to avoid excess of chlorine, which is apt to react upon the salt.

Ferrosesquicyanuret of potassium throws down the following metals, of the annexed colours:—

Titanium . .	Brownish yellow	Silver . .	Orange-yellow
Uranium . .	Reddish brown	Mercury . .	Yellow (both oxides)
Manganese . .	Brownish gray	Tin . . .	White
Cobalt . . .	Dark red-brown	Zinc . . .	Orange
Nickel . . .	Yellowish brown	Bismuth . .	Yellow-brown
Copper . . .	Dirty yellow-brown		

FERROSESQUICYANIC ACID. HYDROFERRIDCYANIC ACID.—When ferrosesquicyanuret of potassium is added to a solution of lead, no immediate precipitation ensues, but, after a time, brown crystals of *ferrosesquicyanuret of lead* are deposited. When these are dissolved in water and decomposed by sulphuretted hydrogen, the filtered solution, which is of a red colour, yields, on evaporation, brown crystals, which are acid, and which bear the same relation to ferrosesquicyanogen, as the corresponding product of the ferrocyanuret of lead does to ferrocyanogen. Liebig represents this acid by the formula $(6\text{cy} + 3\text{fe}) + 3\text{h}$.

FERROSESQUICYANURET, FERRICYANURET, or FERRIDCYANURET OF IRON. PRUSSIAN BLUE.—This celebrated pigment was accidentally discovered by Diesbach, a colour-maker at Berlin, in the year 1710: the first description of the mode of preparing it is given by Woodward in the *Philosophical Transactions* for 1724. It was formerly made as follows. Equal parts of carbonate of potassa and some animal substance, such as dried blood, or horn-shavings, were heated red hot, in a crucible, for half an hour, and 6 or 8 parts of water poured upon the mixture when it had quite cooled. The solution, formerly called *lixivium sanguinis*, was filtered and mixed with a solution containing 2 parts of alum and 1 of protosulphate of iron; a precipitate fell, at first of a dingy-green hue, but which, by copious washings with very dilute hydrochloric acid, acquired a fine blue tint.

At present, Prussian blue is prepared of different degrees of purity, by precipitating solutions of peroxide of iron by ferrocyanuret of potassium, various additions being made to it according to the purposes for which it is required. *Pure Prussian blue* is obtained by adding a solution of ferrocyanuret of potassium to persulphate of iron, thoroughly washing the precipitate, first with water slightly acidulated by sulphuric acid, and then with pure water, and ultimately drying it in a warm place. Liebig recommends the following process on the authority of Hochstätter:—Dissolve 6 parts of protosulphate of iron and 6 parts of ferrocyanuret of potassium, each separately, in 15 parts of water; mix the two solutions, and add to them 1 part of concentrated sulphuric, and 24 of hydrochloric acid, under constant stirring. After some hours, add a clear solution of 1 part of chloride of lime in 80 of water, in successive portions, taking care to stop as soon as any chlorine escapes by effervescence. After some hours, the precipitate should be thoroughly washed, and dried either at common or higher temperatures. The finest product is obtained by washing the precipitate with dilute nitric acid.

Prussian blue is of a peculiarly rich and intense blue, with a copper tint upon its surface: it is insipid, inodorous, insoluble in water, in alcohol, and in dilute acids, and is not poisonous. Concentrated sulphuric

acid forms with it a white pasty mass, from which water again separates it unaltered; nitric acid decomposes it; concentrated hydrochloric acid ultimately abstracts part of its iron. Sulphuretted hydrogen, and iron and zinc filings render it white, in consequence of the abstraction of part of its cyanogen. The alkalis decompose it into soluble ferrocyanurets and protoxide of iron, hence, as a dyeing material it does not resist the action of soap. Boiled in water with peroxide of mercury, it forms bicyanuret of mercury, and an insoluble compound of cyanuret and oxide of iron. According to Chevreul, Prussian blue becomes white in the direct rays of the sun, but regains its blue colour in the dark. It is occasionally used in the composition of writing fluids, and forms the basis of Mr. Stephens's blue ink, in which it is said to be held in solution by oxalic acid. It is extremely hygrometric, and after having been well dried, speedily attracts moisture. When subjected to destructive distillation, it yields a little water and hydrocyanate of ammonia, and then carbonate of ammonia, and a black carburet of iron remains in the retort.

Prussian blue is regarded as a compound of cyanogen and iron, but various views have been taken of its atomic constitution, according as it has been considered a cyanuret, or a hydrocyanate; that is, as containing or not containing elementary water. From the researches of Berzelius, it appears, if considered as anhydrous, or merely retaining adventitious water, to be constituted of

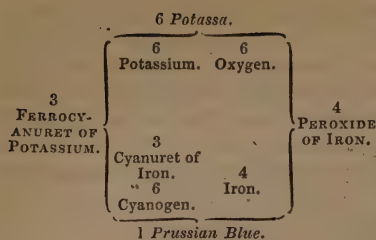
Sesquicyanuret of iron	4	268	62·3
Cyanuret of iron	3	162	37·7
	<hr/>	<hr/>	
	1	430	100·0

Or, of	Iron	7	196	45·6
	Cyanogen	9	234	54·4
		<hr/>	<hr/>	
		1	430	100·0

The *ultimate elements*, therefore, of anhydrous Prussian blue, are

Iron	7	196	45·6
Carbon	18	108	25·1
Nitrogen	9	126	29·3
	<hr/>	<hr/>	
	1	430	100·0

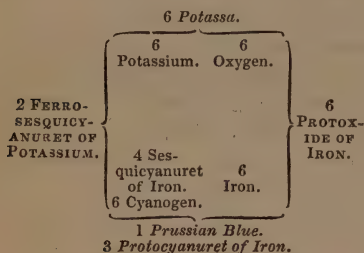
Assuming Prussian blue to be a compound of 4 atoms of sesquicyanuret of iron, and 3 of cyanuret of iron, we see why it is produced by the action of ferrocyanuret of potassium (consisting of cyanuret of potassium and cyanuret of iron) upon the salts of *peroxide* of iron: for an interchange of elements takes place between the cyanuret of potassium and *peroxide* of iron, by which potassa and *sesquicyanuret* of iron are formed. Let us suppose (to avoid fractions) that 3 atoms of ferrocyanuret of potassium (containing 6 atoms of cyanuret of potassium and 3 of cyanuret of iron) act upon 4 atoms of peroxide of iron (containing 4 atoms of iron and 6 of oxygen). In this case, the 6 of potassium (in the ferrocyanuret) combine with the 6 of oxygen (in the peroxide of iron) to form 6 atoms of potassa; and the 4 of iron (in the peroxide) unite to the 6 of cyanogen (in the cyanuret of potassium) to form 4 atoms of *sesquicyanuret of iron*, which, by combining with the 3 of cyanuret of iron,



(left by the ferrocyanuret of potassium,) form *Prussian blue*. The whole result will, perhaps, be more explicit in the annexed diagram, which shows that the iron of the peroxide takes the place of the potassium of the ferrocyanuret. (The annexed numbers refer to atoms or equivalents, as will be evident from the foregoing tables of composition.)

It will also be obvious that *protoxide* of iron cannot form Prussian blue, but that when it exchanges elements with ferrocyanuret of potassium, *protocyanuret* of iron and not sesquicyanuret, must be the result. When, on the other hand, *ferrosesquicyanuret of potassium* is mixed with a *protosalt* of iron, potassa and cyanuret of iron are the new products; the former unites with the acid previously in combination with

the protoxide, and the cyanuret of iron is partly precipitated, and partly unites to the sesquicyanuret of iron contained in the ferrosesquicyanuret of potassium, to form Prussian blue: this will be evident from the annexed diagram, referring at the same time to the above tables of the composition of Prussian blue, and of the ferrosesqui-



cyanuret of potassium*. Liebig observes, in reference to the composition of Prussian blue, that it cannot be obtained anhydrous without decomposition, so that one is forced to consider it as a combination of hydroferrocyanic acid and sesquioxide of iron, in which the elements have not undergone reduction.

SOLUBLE PRUSSIAN BLUE.—It is often remarked, that under certain circumstances of precipitation, Prussian blue becomes apparently soluble

* Mr. Graham describes the blue precipitate which falls on adding the ferrosesquicyanuret of potassium (and which, in the above diagram, is represented as a mixture of cyanuret of iron and Prussian blue) under the name of *ferricyanide of iron*, or *Turnbull's blue*. "The same blue precipitate may," he adds, "be obtained by adding to a protosalt of iron a mixture of yellow prussiate of potash, chloride of soda, and hydrochloric acid. The tint of this blue is lighter and more delicate than that of Prussian blue. It is occasionally used by the calico-printer, who mixes it with permuriate of tin, and prints the mixture, which is in a great measure soluble, upon Turkey-red cloth, raising the blue colours afterwards by passing the cloth through a solution of chloride of lime

containing an excess of lime. The chief object of that operation is indeed different, namely, to discharge the red and produce white patterns, where the acid is printed upon the cloth; but it has also the effect incidentally of precipitating the blue pigment and peroxide of tin together on the cloth, by neutralizing the acid of the permuriate of tin. This blue is believed to resist the action of alkalis longer than ordinary Prussian blue. Mr. R. C. Campbell observed that the ferricyanide of iron may be distinguished from Prussian blue by the circumstance, that when boiled in a solution of yellow prussiate of potash, it affords red prussiate of potash, which dissolves, and a gray insoluble residue of ferrocyanide of iron and ferrocyanide of potassium. (LIEBIG.)"

in water; this is especially the case when a persalt of iron is added to excess of a solution of ferrocyanuret of potassium. In this case, a compound is formed between the Prussian blue and the ferrocyanuret, soluble in pure water, but insoluble in saline solutions; accordingly, as soon as the salts are washed out of the precipitate, it begins to dissolve in the water. This compound, according to Berzelius (*Ann. de Ch. et Ph.*, li.), consists of 1 atom of ferrocyanuret of potassium and 1 of Prussian blue.

FERROCYANURET OF POTASSIUM AND IRON.—This name is given by Liebig to the bluish-white precipitate which falls when ferrocyanuret of potassium is added to a protosalt of iron. By the action of chlorine or nitric acid, 3 equivalents of potassium and 1 of iron are abstracted from 3 equivalents of the compound, and Prussian blue remains.

PROTOSULPHOCYANURET OF IRON.—The sulphocyanic acid dissolves iron with the evolution of hydrogen, and a pale-green solution is obtained, which may be evaporated to dryness in vacuo, but deposits a yellow sediment on exposure to air.

PERSULPHOCYANURET OF IRON.—This compound may be obtained in the form of a deliquescent uncrystallizable mass, of a red colour, by dissolving hydrated peroxide of iron in sulphocyanic acid, and carefully evaporating to dryness. When sulphocyanic acid is added to any soluble persalt of iron, it produces a very characteristic red tint, and thus applied, is a delicate and useful test.

BORURET OF IRON.—A compound of boron and iron results from the action of hydrogen at a red heat upon borate of iron. (LASSAIGNE.) According to Arfwedson, the boracic acid is not susceptible of such decomposition.

PROTOBORATE OF IRON is an insoluble powder, obtained by adding a solution of borate of soda to one of protosulphate of iron.

PERBORATE OF IRON is of a yellow colour, and insoluble. It is formed by adding borate of soda to persulphate of iron: it is vitrifiable at a high heat.

ALLOYS OF IRON.—*Iron and Potassium* form a white soft alloy which effervesces in water. When a mixture of charcoal, iron-filings, and magnesia, is exposed to its fusing heat, the resulting globule contains traces of *magnesium*. With lime no analogous effect ensues. The alloy of *iron and manganese* is white, hard, and brittle, and sometimes by its presence confers peculiar characters on steel. A little iron in manganese renders it magnetic, and diminishes its tendency to oxidizement.

CHARACTERS OF THE SALTS OF IRON.—1. *Protosalts.* The salts of the protoxide of iron are of a green or bluish-green colour; they have an astringent and sometimes slightly sweet taste, but exert an acid reaction on moistened litmus; they are mostly soluble in water, and all soluble in dilute hydrochloric acid; their aqueous solution absorbs nitric oxide, yielding a dark olive or almost black liquid which rapidly absorbs oxygen. Ferrocyanuret of potassium (yellow prussiate of potash) gives a white precipitate in those salts when they are perfectly free from protoxide, which becomes blue by exposure to air, or by the addition of nitric acid

or chlorine; but with ferrosesquicyanuret of potassium (red prussiate of potash) they immediately become deep blue. Infusion of galls, added to a weak solution of a pure protosalt of iron, does not produce discoloration, but on exposure to air, or on the addition of a drop or two of solution of ammonia, the liquid becomes purple. When the aqueous solutions of these salts are exposed to air, they deposit a yellow-brown powder which is often a subsalt of peroxide of iron. The double chloride of sodium and gold is an extremely delicate test of the protosalts of iron. A grain of protosulphate of iron, with an equal weight of carbonate of soda, dissolved in four pints of water, produces a precipitate, gradually becoming purple on the addition of a drop of solution of chloride of gold: without the carbonate of soda, the effect did not appear in less than three days. (FICINUS, *Quart. Journ.*, xv. 382.)

2. *Persalts*.—The soluble salts of the peroxide of iron have an acid reaction, a very astringent and often acid taste, and a brown colour; those which are insoluble in water are soluble in hydrochloric acid; they give black precipitates with infusion of galls and blue with ferrocyanuret of potassium, but if the solution be very dilute, and oxalic acid or an oxalate present, this test is ineffective, owing to the solubility of Prussian blue in oxalic acid. Some of these salts, and especially the perchloride and persulphate, are rendered of a peculiar blood-red colour, and furnish a red precipitate, when the solutions are concentrated, upon the addition of sulphocyanic acid and the soluble sulphocyanates: a very similar discoloration is effected by the meconic acid and the soluble meconiates, and by tinctures of opium. The effects may, to a certain extent, be distinguished by the addition of a few drops of chloride of gold, which destroys the tint occasioned by sulphocyanic compounds, but produces little effect upon those of the meconic acid. The indigotic acid also renders the persalts of iron of a red colour.

None of the metals precipitate iron in a metallic state, if we except zinc and cadmium, which effect an imperfect precipitation, especially from some of its protosalts, in vessels excluded from the access of air. Before the blowpipe, peroxide of iron produces with microcosmic salt, or borax, in the exterior flame, a glass, which is blood-red while hot, but yellow when cold. The protoxide forms with these fluxes a green glass, which, by increasing the proportion of the oxide, passes through bottle-green to black, and is opaque. The glass from the peroxide becomes green in the interior flame, and is reduced to protoxide, and becomes attractable by the magnet. When placed on the wick of a candle, it burns with the crackling noise peculiar to iron.

MANUFACTURE OF IRON AND STEEL.—It has already been stated that the nodular argillaceous carbonated iron-ore of the coal formation, is chiefly resorted to in this country as the source of the metal; the following is an outline of the process of reduction. (AIKIN'S *Dictionary; Supplement to the Encyclopædia Britannica*; LARDNER'S *Cyclopædia*; DUMAS, *Chimie app. aux Arts*.)

The first process that the ore undergoes after it has been broken into small pieces, is *roasting*. This is performed as follows:—Upon an

oblong piece of firm and level ground is laid a bed of small coal, from four to eighteen inches thick; upon this is placed a stratum of ironstone, from eighteen inches to two feet thick, the upper surface of which is rendered more compact by filling up the interstices with smaller pieces. Upon this rests a layer of small coal not more than two inches thick, and on this, as a base, is reared a gradually-diminishing pile of ore; finally, the whole external surface receives a complete covering of small coal and coal-dust. The pile is kindled by applying burning coals to the lower stratum. The breadth of the pile at the bottom varies from ten to sixteen feet, the usual height is about five feet, and the length varies from thirty feet to sixty yards. When the coals are consumed, the pile gradually cools, and in eight or ten days may be wheeled away to the furnace. The ore, if well roasted, will now be of a reddish-brown colour, of diminished specific gravity, and will have become magnetical; the sulphur, water, inflammable matter, and carbonic acid, that it originally contained, will have been dissipated, and it is now ready to be *smelted*. The *smelting-furnace* resembles externally a truncated quadrilateral pyramid of considerable height in proportion to its thickness; it is built of strong masonry, with contrivances to obviate the danger of its cracking by the expansion that takes place when it is heated. The interior of the furnace consists of the five following parts, reckoning from the bottom upwards. The *hearth*, composed of a single block of quartz-grit about two feet square: upon this is erected what in France and Germany is called the *crucible*, which is a four-sided cavity six feet six inches high, slightly enlarging upwards so as to be two feet six inches square at the top: the part above, called the *boshes*, is in the shape of a funnel or inverted cone, eight feet in perpendicular height, and twelve feet in diameter at the top; this terminates in the *cavity* of the furnace, which is of a conical figure, thirty feet high, and three feet diameter at the top; from this part it enlarges into a funnel-shaped *chimney*, about eight feet high, and sixteen in diameter at its mouth. About two feet above the hearth is a round aperture, called the *Tuyere*, or *Tweer*, made in one of the sides of the crucible to admit the extremity of the blast-pipe, through which the air in a high state of compression is forced into the furnace, and at the bottom of the crucible is an aperture, through which the scoræ and melted metal are from time to time discharged. A furnace of this construction, if it meets with no accident, may be kept in constant work for three years or more without requiring any repairs. The furnace is charged at the chimney, by regular intervals, with coke, iron-ore, and limestone, in the proportion of about four of the first, three and one-third of the second, and one of the third, by weight, care being taken so to regulate the frequency of the charges, as that the furnace shall be always full nearly to the top of the great cavity. The density of the blast and the form of the discharging-pipe are ordered so that the chief focus of heat is about the bottom of the boshes; hence the ore has to descend about thirty-eight feet perpendicular, before it arrives at the place where the fusion is effected. This does not happen in less than forty-eight hours; so that the ore is all this time in a state of cementation at a high temperature, in contact with the burning fuel, and, in consequence, is almost saturated with carbon when it reaches the hottest part of the furnace. Being arrived at this place, the limestone

flux, and the earthy particles of the coke and ore, run down into a slag*; the iron is also melted, and more or less decarbonized, and in part oxidated by the blast, inversely, according to the proportion of fuel with which it is mixed. The fluid mass soon sinks down below the influence of the blast, and while it remains quiet at the bottom of the furnace, the globules of iron are precipitated from the slag, and occupy the lowest place, while the covering of scorïæ thus interposed between the metal and that portion of the blast which is reflected downwards, prevents it from suffering any further loss of carbon. In proportion as the melted matter accumulates, the slag being the uppermost flows out at the aperture made for this purpose: the iron is let out at regular intervals, into furrows made in sand, where it forms what is called *pig-iron*; or into a large reservoir, whence it is poured by means of ladles into moulds, forming all the various articles of *cast-iron* ware.

The following are some of the circumstances in the smelting which influence the quality of the produce. Much depends on the *fuel*: if the coke is not perfectly made, but retains bitumen, the whole mass cakes in the upper part of the furnace, and instead of descending regularly to the focus of heat, falls down at irregular intervals, so that part of the metal is detained too long before the blast, and decarbonized and oxidated, while other portions pass so rapidly through the furnace as never to be thoroughly reduced; hence the amount of the produce is diminished, and its quality deteriorated. Nor is it of less importance that the coke should be dry when put into the furnace. The *proportion of fuel* should also be adapted to the richness of the ore, so that there may be sufficient both to keep up the necessary degree of heat, as well as to carbonize the metal: hence, as the charges of ore and fuel are always proportioned by measure, if an ore somewhat richer than usual happens accidentally to be employed without a corresponding addition of fuel, the produce, though somewhat increased in quantity, will be more than equivalently reduced in quality. Another circumstance that the manufacturer must carefully attend to, is the proper choice of ore with regard to *fusibility*; for, as it is not only requisite that the iron should be melted, but also highly carbonized, and as coke gives off its carbon more difficultly than charcoal, a very fusible ore would melt long before it arrived at the focus of the furnace, and passing rapidly through, would reach the hearth without having had time to imbibe the proper quantity of carbon. Hence it is, that the rich *hæmatites*, although they afford an excellent quality of iron when smelted with charcoal, produce nothing but white iron when treated in the coke-furnace; while, on the other hand, *argillaceous ironstone* being much more refractory, does not melt till it comes into the very hottest part of the furnace, and therefore has had full time to absorb the desirable quantity of carbon.

Another thing to be attended to, is the *proper regulation of the*

* The *slag* chiefly consists of silica in combination with lime, alumina, magnesia and the protoxides of manganese and iron. According to Mitscherlich (*Ann. de Ch. et Ph.*, xxiv.), it frequently consists of a bisilicate of lime and magnesia with more or less protoxide of iron: and

this compound even forms crystals resembling *pyroxene*. The production of *artificial minerals* by these processes, is a subject of extreme interest and importance, both in a geological and chemical view, and an excellent field for experimental inquiry.

blast, and this depends upon its dryness, its temperature, its compression, and its direction. The dryness and temperature appear to be principally governed by the season of the year. The drier and colder the air is, the greater will be its effect on the combustion; and it is found that the produce of iron during the summer months, is inferior in quantity and quality to that which is manufactured in the winter: a clear, dry, and severe frost is the most favourable period in every respect for the working of the furnace, and a change to snow or rain is followed by a corresponding deterioration. The higher the temperature of the blast when it is delivered into the furnace, the smaller will be the quantity of oxygen contained in every cubic foot, and, of course, the vigour of the combustion*. Nor is the force of the blast and its direction a subject of less importance; it is obvious, that in proportion as the charge descends,

* Since this account of the manufacture of iron was written, an important change has been suggested in the introduction of the blast, in consequence of the discovery by Mr. Neilson, of Glasgow, of the saving of fuel and improvement in the iron, by sending a blast of *hot*, instead of cold, air, into the furnace. A notice of this discovery is given by Dr. Clark (*Edin. Phil. Trans.*, xiii.), of which the following is an abstract. The improvement consists in *heating* the air in its passage from the blowing-machines to the furnace, and the following are the results of this system, obtained in the Clyde Iron-Works.

During the first six months of 1829, when all the cast-iron in the Clyde Iron-Works was made by the cold blast, a ton of cast iron required for fuel to reduce it, 8 tons $1\frac{1}{2}$ cwt. of coal, converted into coke. During the first six months of the following year, when the air was heated to near 300° Fahr., one ton of cast-iron required 5 tons $3\frac{1}{4}$ cwt. of coal, converted into coke. The saving amounts to 2 tons 18 cwt. on the making of one ton of cast-iron; but from that saving comes to be deducted the coals used in heating the air, which were nearly 8 cwt. The net saving thus was $2\frac{1}{2}$ tons of coal on a single ton of cast-iron. But during that year, 1830, the air was heated no higher than 300° Fahr. The great success, however, of those trials, encouraged the iron-masters to try the effect of a still higher temperature. Nor were their expectations disappointed. The saving of coal was greatly increased, so that, in 1831, Mr. Dixon, of Calder Iron-Works, attempted the substitution of raw coal for coke. The attempt was successful; and, since that period, the raw coal has been adopted in the majority of the Scotch iron-works.

The temperature of the air under blast had now been raised so as to melt lead, and sometimes zinc, and therefore was above 600° Fahr., instead of being only 300° , as in the year 1830. It became, in consequence, so much elevated in temperature as to require the adoption of an old invention called the *water-tweezer*, which consists in surrounding the tuyere with water. The water is kept continually changing as it heats, by means of one pipe to admit the water cold, and another to let it escape when heated.

During the first six months of the year 1833, when all these changes had been fully brought into operation, one ton of cast-iron was made by means of 2 tons $5\frac{1}{4}$ cwt. of coal, (not previously converted into coke.) Adding to this, 8 cwt. of coal for heating, we have 2 tons $13\frac{1}{4}$ cwt. of coal required to make a ton of iron; whereas, in 1829, when the cold blast was in operation, 8 tons $1\frac{1}{2}$ cwt. of coal had to be used. This being almost exactly three times as much, we have, from the change of the cold blast to the hot, combined with the use of coal instead of coke, *three times as much iron made from any given weight of splint coal*. The efficacy of a given quantity of air, in the production of iron, is also greatly increased, and the requisite proportion of flux diminished.

In regard to the *cause* of the above results, Dr. Clark observes, that it is necessary to discriminate between the quantity of fuel consumed, and the temperature produced. For instance, we may conceive a stove at the temperature of 500° and lead put into it to melt. Then, since the melting-point of lead is more than 100° higher, it is evident that whatever fuel might be consumed in keeping that stove at 500° , is consumed

the carbonaceous matter is continually diminishing; hence the proper situation for the focus of the blast is that part of the furnace, where, when the ore shall have arrived, it will be fully carbonized and surrounded with a sufficient quantity of fuel to excite an intense heat, and absorb nearly the whole of the oxygen of the air, and thus prevent it from either oxidating the iron, or carrying off the carbon with which it may be combined. This precise situation, in a furnace properly constructed, will be found to be just within the expansion of the boshes; but as this is more than four feet above the tuyere hole, the blast must be delivered with great velocity, and in a direction somewhat slanting upwards, in order that it may be reflected by the opposite wall of the crucible, and arrive at its proper place without undergoing any material decomposition. When the blast enters too rapidly, and in too concentrated a state, it renders the line of its passage, before it is reflected, so cool, that the descending slag which comes within its influence is suddenly solidified, and blown into a tube, reaching, perhaps, half-way across the crucible, through which the blast continues to rush; and in consequence of this protection, is conveyed with greater precision, and in a less decomposed state, into the upper part of the furnace. If, after this, the compression of the air is somewhat diminished, the tube still remains firm, often for days together, and the furnace works in the best manner. But, on the other hand, when too

to no purpose. In the manufacture of cast-iron likewise, a certain temperature is required to work the furnace favourably, and all the fuel consumed to produce any *lower* degree of temperature, is consumed in vain. How the hot blast increases the *temperature* of a furnace, will appear on adverting to the relative weights of the solid and gaseous materials used in the reduction of iron. As nearly as may be, a furnace, as wrought at Clyde Iron-Works, had two tons of solid materials an hour put in at the top, and this supply was continued for 23 hours a-day; one half-hour every morning and evening, being consumed in letting off the iron. But the gaseous material—the hot air—what might be the weight of it? This can easily be ascertained thus: I find, by comparing the quantities of air consumed at Clyde and at Calder Iron-Works, that one furnace requires of hot air from 2500 to 3000 cubical feet in a minute. I shall here assume 2807 cubical feet to be the quantity; a number that I adopt for the sake of simplicity, inasmuch as, calculated at an avoirdupois ounce and a quarter, which is the weight of a cubical foot of air at 50° Fahr., these feet correspond precisely with 2 cwt. of air a minute, or *six tons an hour*. Two tons of solid material an hour, put in at the top of the furnace, can scarce hurtfully affect the

temperature of the furnace, at least in the hottest part of it, which must be far down, and where the iron, besides being reduced to metal, is melted, and the slag too produced. When the fuel put in at the top is coal, I have no doubt that, before it comes to this far-down part of the furnace, the place of its useful activity, the coal has been entirely coked; so that, in regard to the fuel, the new process differs from the old more in appearance than reality. But if two tons of solid material an hour, put in at the top, are not likely to affect the temperature of the hottest part of the furnace, can we say the same of six tons of air an hour, forced in at the bottom near that hottest part? The air supplied is intended, no doubt, and answers to support the combustion; but this beneficial effect is, in the case of the cold blast, incidentally counteracted by the cooling power of six tons of air an hour, or two cwt. a minute, which, when forced in at the ordinary temperature of the air, cannot be conceived otherwise than as a prodigious refrigeratory passing through the hottest part of the furnace, and repressing its temperature. The expedient of previously heating the blast obviously removes this refrigeratory, leaving the air to act in promoting combustion, without robbing the combustion of any portion of the heat it produces. (See Dr. Clark's paper.)

loose and soft a blast is admitted, and more especially if it is charged with moisture, it is unable to reach the top of the crucible without being decomposed, and the reflection which it undergoes from the wall of the crucible, weakens and disperses it to such a degree, that the combustion which ought to take place within the boshes, now occupies the whole upper part of the crucible: in consequence of this, the tube of scoriæ is presently burnt away, the iron, almost as fast as it is melted, is ignited and oxidized, the tuyere-hole glows, like the sun, with an intensely vivid white light; the scoriæ, from being yellowish-white streaked with blue, become green, brown, and finally black, nearly the whole of the iron in the state of oxide being taken up by it; the blocks of refractory gritstone, with which the lower part of the furnace is lined, are worn into great holes, and in the space of a few hours prodigious damage is sustained. (AIKIN'S *Dictionary*, Art. IRON.)

VARIETIES OF IRON.—An extremely important part of the chemical history of iron relates to the varieties of the metal which are found in commerce. These are much too numerous to be dwelt upon here; so that we shall limit our observations to the principal of them only, which are *cast-iron*, *wrought-iron*, and *steel*.

CAST-IRON is essentially a *subcarburet*. There are two principal varieties of it, distinguished by the terms *white* and *gray*. *White cast-iron* is very hard and brittle, and, when broken, of a radiated texture. Acids act upon it but slowly, and exhibit a texture composed of a congeries of plates, aggregated in various positions. (DANIELL, *Quarterly Journal of Science and Arts*, vol. ii., p. 280.) *Gray* or *mottled-iron* is softer and less brittle: it may be bored and turned in the lathe. When immersed in dilute hydrochloric acid, it affords a large quantity of black insoluble matter, which Mr. Daniell considers as a triple compound of carbon, iron, and silicium, and which has some very singular properties. The texture of the metal resembles bundles of minute needles. This variety of iron is occasionally substituted for wrought-iron, from its toughness and comparative purity; it sometimes contains only 3 or 4 per cent. of foreign matter. Beams, employed in building, and various parts of machinery which formerly were exclusively made of wrought-iron, are now cast. A curious operation is often performed upon small articles made of cast-iron, in order to convert them into malleable iron, which is termed *decarbonization*, and is sometimes practised upon steel: it consists in bedding the articles in powdered oxide of iron (*hæmatite* is generally used), and exposing them to a red heat: the carbon is thus abstracted from the cast-iron, and it becomes as flexible and malleable as wrought-iron.

The following are the analyses of three samples of the best gray cast-iron, from the furnaces of South Wales, by Gay Lussac.

	I.	II.	III.
Carbon . .	2·450 . .	2·550 . .	1·666
Silicium . .	1·629 . .	1·200 . .	3·000
Phosphorus .	0·780 . .	0·440 . .	0·492
Manganese .	a trace . .	a trace . .	a trace
Iron . . .	95·150 . .	95·810 . .	94·842
	100·000	100·000	100·000

In some foreign cast-iron the proportion of manganese is much more considerable, amounting to from 2 to 5 per cent. It will be obvious, by a reference to the composition of steel, that if the process of decarbonization be not carried to its full extent, cast-iron may thus be converted into steel; and what is termed *natural steel* is in fact steel so obtained.

WROUGHT-IRON.—Cast-iron, after it has been to a certain extent *refined*, by fusion in a forge, in contact with charcoal, is in this country converted into wrought-iron by a curious process, called *puddling*. The cast-iron is put into a reverberatory furnace, and when in fusion is stirred, so that every part may be exposed to the air and flame. After a time the mass heaves, emits a blue flame, and gradually grows tough, and becomes less fusible, and at length pulverulent; the fire is then urged, so that the particles again agglutinate at a welding-heat, and are gradually wrought up into masses. In that state of intense heat the masses are passed successively between rollers, by which a large quantity of extraneous matter is squeezed out, and the iron becomes malleable. The bars, into which it is formed, are cut into pieces, placed in parcels in a very hot reverberatory, and again hammered, or rolled out into bars. They are thus rendered more tough, flexible, and malleable, but much less fusible, and may be considered as nearly *pure iron*.

STEEL.—This extraordinary and valuable substance is a compound of iron with a small relative proportion of carbon*, which varies in the varieties of steel. Other substances are also occasionally present, which apparently modify some of its characters: traces of phosphorus, sulphur, and manganese, are not uncommon. It combines the fusibility of cast with the malleability of bar-iron, and when heated and suddenly cooled it becomes very *hard*, but may again be softened by the careful management of heat; hence its superiority for the manufacture of cutting instruments, and an almost infinite number of useful purposes in the arts. If kept for a long time in fusion it loses carbon, and becomes pure iron. Its texture, when examined by the action of an acid, is not fibrous, but lamellated.

Iron is converted into steel by a process called *cementation*, which consists in heating bars of the *purest* iron in contact with charcoal; it

* The identity of charcoal and diamond above adverted to, receives additional proof by the conversion of iron into steel when that metal is ignited with diamond powder. Upon this subject some controversy will be found in the *Phil. Mag.*, vol. v.; the *experimentum crucis* is, however, due to Mr. Pepys, who availed himself of Mr. Children's Voltaic battery of large plates for the production of the requisite heat (*Phil. Trans.*, 1815, p. 371): he bent a wire of pure soft iron so as to form an angle in the middle, in which part he divided it longitudinally by a fine saw; in the opening so formed he placed diamond-powder, securing it in its situation by two finer wires, laid above and below it, and kept from shifting by

another small wire, bound firmly and closely round them. All the wires were of pure soft iron, and the part containing the diamond-powder was enveloped by thin leaves of talc. Thus arranged, the apparatus was placed in the electrical circuit, where it was kept red-hot for six minutes: on opening the wire the diamond had disappeared, the interior surface of the iron had fused into numerous cavities, notwithstanding the very moderate heat to which it had been exposed, and all that part which had been in contact with the diamond was converted into perfect blistered-steel. A portion of it being heated red and plunged into water, became so hard as to resist the file and to scratch glass.

absorbs carbon and increases, according to Mushet, in weight*, at the same time acquiring a *blistered* surface. That carbon is vaporizable, and that it may enter into and combine with the iron in the form of vapour, appears probable from the experiments of Le Play and Laurent (*Ann. de Ch. et Ph.*, lxxv. 417); yet it is often doubtful how far any carbon is actually absorbed in the common process of steel-making, for we never find wrought-iron absolutely free from carbon, and often it seems rather to lose than gain it; perhaps therefore some more intimate union between the carbon and iron is effected by cementation, for it is scarcely possible that a mere change in the mechanical texture of the iron can give it the properties of steel, and Pepys's experiment with iron and diamond, referred to in the note to the preceding paragraph, is in favour of actual carbonization.

When blistered-steel is drawn down into smaller bars and beaten, it forms *tilted-steel*; and this broken up, heated, welded, and again drawn out into bars, forms *shear-steel*. *English cast-steel* is prepared by fusing blistered-steel with a flux composed of carbonaceous and vitrifiable ingredients, casting it into ingots, and afterwards, by gentle heating and careful hammering, or rolling, giving it the form of bars.

By comparing the analysis of blistered-steel with that of cast-steel, it would appear that in the intense heat to which the metal is necessarily subjected for its fusion it loses silicium and a little carbon; but the great superiority of cast-steel for many of the purposes of the arts, no doubt depends upon its comparative uniformity of composition. The following are analyses of three samples of blistered-steel by Vauquelin, and four of cast-steel by Gay Lussac.

Blistered-Steel.				Cast-Steel.			
Carbon . .	0·79	0·68	0·63	0·62	0·65	0·65	0·94
Silicium . .	0·15	0·12	0·11	0·03	0·00	0·04	0·08
Phosphorus .	0·34	0·82	1·52	0·03	0·08	0·07	0·11
Iron . . .	98·72	98·38	97·74	99·32	99·27	99·24	98·87
	100·00	100·00	100·00	100·00	100·00	100·00	100·00

It appears probable that the proportion of carbon in the above analyses must be somewhat underrated: the first column of Gay Lussac's table gives the components of the best English cast-steel, and the two last that of French steel of first and second quality. My experience in the use of steel for the manufacture of dies for coinage has been very considerable, and the denomination of steel which we prefer for that purpose at the

* The following table, drawn up by Mr. Mushet, shows the quantities of charcoal which disappeared during the conversion of iron into the different *subcarburets of iron* known in commerce. (*Phil. Mag.*, xiii.)

When the carbon amounts to $\frac{1}{60}$ of the whole mass, the hardness is at a maximum.

Charcoal absorbed.

RESULTS.

$\frac{1}{20}$ --- soft cast-steel.

$\frac{1}{10}$ --- common cast-steel.

$\frac{1}{6}$ --- the same, but harder.

$\frac{1}{3}$ --- the same, too hard for draw-

$\frac{1}{2}$ --- white cast-iron. [ing.

$\frac{2}{3}$ --- mottled cast-iron.

$\frac{1}{5}$ --- black cast-iron.

Mint, approximates, as far as the few specimens which I have examined enable me to infer, to the composition given in the last column; at least, when the carbon has fallen short of 1 per cent. I have found it deficient in hardness, and when it has exceeded 1 per cent. the dies have split under the multiplying press, or if hardened, have not stood to their work in the coining presses. But the quality of steel is doubtless much influenced by minute proportions of other bodies, and unless it contains a sensible quantity of phosphorus it cannot be depended upon for the manufacture of dies, though I have not been able to satisfy myself of the exact requisite relative proportion. The trials to which steel is subjected, under the form of coining-dies, are extremely rigorous, and its mechanical as well as its chemical characters greatly influence its fitness for the purpose; but it would occupy too much space here to enter into detail upon these matters, which are in a great measure foreign to our present subject.

WOOTZ, or INDIAN STEEL, which has, by some, been considered as superior to any other, for the purpose of making certain edge-tools, apparently derives its peculiar excellence from combination with a minute portion of aluminum and silicium. (*Quart. Jour. of Science*, vii. 288.) Whether these substances are in the ore, or are furnished by the crucible used in making the steel, is not certainly known. Wootz, in the state in which it is imported, is not fit to make into fine cutlery; it requires a second fusion, by which the whole mass is purified and equalized, and fitted for forming the finest edge-instruments.

CASE-HARDENING is an operation performed upon cast or wrought-iron, by which it is superficially converted into steel: the article is for this purpose either heated to redness in a crucible, or vessel containing charcoal powder; or sometimes, if small and delicate, is wrapped round with leather, and then gradually heated to redness, and kept in that state till its surface is duly carbonized. Ferrocyanuret of potassium is also a valuable material as a case-hardener, and in various operations connected with the management of steel.

HARDENING AND TEMPERING STEEL.—When steel is heated to a cherry-red colour, and then plunged into cold water, it becomes so extremely hard and brittle, as to be unfit for almost any practical purpose. To reduce it from its extreme hardness, is called by the workmen *tempering*, and is effected by again heating the steel to a certain point. The surface being a little brightened, exhibits, when heated, various colours, depending upon the formation of thin films of oxide*, which constantly change as the temperature is increased, and by these colours it has been customary to judge of the temper of the steel. But a more accurate, as well as convenient method, is to use a bath and thermometer; the bath may be of mercury, or of the fusible mixture of lead, tin, and bismuth, or, indeed, of any fluid whose boiling-point is not much

* That the colour produced on the surface of heated steel is the effect of oxidation, is proved from the circumstance that when steel is heated and suffered to cool under mercury or oil, none of the colours appear; nor do they when it is heated in hydrogen or nitrogen.

under 600° . Into this bath the articles to be tempered are put, together with the bulb of a thermometer graduated to the boiling-point of mercury. The corresponding *degrees* at which the various colours appear are from 430° to 600° . The first change is at about 430° , but this is too faint to be distinguished, except by comparison with another piece of untempered polished steel. At 460° the colour is *straw*, becoming deeper as the temperature is increased; at 500° the colour is *brown*; this is followed by a *red* tinge with streaks of *purple*, then *purple*, and at nearly 600° it is *blue*. The *degrees* at which the respective colours are produced being thus known, it follows that the workman has only to heat the bath, with its contents, up to the required point. For example, suppose the blade of a penknife (or one hundred of them) to require tempering: they are suffered to remain in the bath until the mercury in the thermometer rises to 460° , and no longer, that being the heat at which the knife (supposing it to be made of the best English cast-steel) will be sufficiently tempered. The advantages attending this method are obvious; the heat is equally applied to the whole; and the workman, instead of attending to the colour of each blade, has only to observe the thermometer.

It has been found that steel, for certain uses, is sufficiently tempered long before it is heated to produce any change of colour, a circumstance which gives additional value to the process by a thermometer. The knife-edges attached to a pendulum described by Capt. Kater (*Phil. Trans.*, 1818, p. 38), were forged by Mr. Stodart, from a piece of fine wootz. They were carefully hardened, and tempered in the bath at 430° ; on trial they were found too soft. They were a second time hardened, and then heated to 212° . The intention was to increase the heat from that point, trying the temper at the advance of about every ten degrees. In the present instance this was not necessary, the heat of boiling water proving to be the exact point at which the knife-edges were admirably tempered. It is highly probable that steel, for many uses, may be sufficiently tempered in a range so extensive as from 212° to 430° , and, by the thermometer, all the intervening degrees may be certainly ascertained. But it is not the temperature only, but also the time during which the steel is exposed to it, which influences its hardness or temper.

What may be the changes effected in the molecular constitution of steel by the operation of hardening is an important, but a very difficult and undecided question; that they are considerable, there can be no doubt, but that they extend beyond mechanical arrangement, and affect chemical composition, according to the notions of Karsten, is a theory which requires much more satisfactory proof than it has hitherto received; nor are the changes which other substances undergo by a similar operation in any way illustrative of or applicable to those of steel, the electromagnetic properties of which are not less remarkable than the coarser mechanical changes which it sustains, and which are in all probability someway related to each other, and to the more abstruse causes of crystalline peculiarities. There is certainly in many points an analogy between unannealed or suddenly cooled glass and tempered or hardened steel, and the extraordinary molecular and crystalline peculiarities of glass, when more correctly understood, may perhaps tend to throw some light

upon the more obscure subject of steel, but as yet this is not the case. It is, however, by no means uncommon to find the same unstable arrangement of particles and inequality of tension in a mass of hardened steel, as in a lump of glass which has solidified in cold water; from the surface to the interior, successive crusts or coats of variable texture and hardness present themselves. Sometimes a steel die, after it has been for some time hardened and apparently safe, will split with an audible report, and its fracture then exhibits a soft core covered by successive coats or layers, increasing in hardness from the centre towards the exterior.

In addition to the difficulties arising out of the mass with which he has to deal, and the changes of texture, if not of composition, which it has necessarily been subjected to in the various operations of perfecting the impression from the punch in the press, the manufacturer of dies for medals or coinage has another obstacle to contend with, which is the necessity of keeping the face or work of the die perfectly clean and free from scales and oxidizement, so that it may not only be without any obvious blemish, but present that peculiar velvety hue which so much enhances the beauty of the subsequent impressions in gold, silver, or copper: to this end the charcoal in which the die is imbedded, when it is heated previous to hardening, must be carefully looked to; it should be animal charcoal, and cyanogen, if present, is rather favourable than otherwise to the ultimate result; moisture, air, potassium, sulphur, and other things sometimes present in charcoal, are injurious; and when the die is at a proper heat and ready to be plunged into the hardening cistern, or submitted to the sudden action of a gush of water, all contact of air with the face of the die must be scrupulously avoided. Protecting pastes are seldom of much use.

The degree of hardness attainable by steel will depend upon the heat to which it had been raised, and the coldness of the water or other medium into which it is plunged; so that when very cold water cannot be procured, the die or other article must be heated proportionately high; a dull red heat into water at 34° , a cherry red into water at 50° , an orange heat into water at 80° , and a dull white heat into water at 100° , produce nearly the same effects; but the real hardness attained in water which is warm never equals that given by cold water: a red heat and water at 45° is the most desirable for die hardening; and although by subsequent tempering the die may, if necessary, be *brought down*, or softened, it is always safest to give it, if possible, its due hardness by the first operation. The risk of injuring the face of a die by oxidizement or scaling, or of *burning* the die, as it is usually called, increases greatly with a high temperature, and this is another reason why, in this particular branch, a moderate heat and very cold water is greatly to be preferred to a higher heat and warmer water. The hardening of steel when in thin bars, or other regular form, and where extreme cleanliness of surface is dispensed with, is comparatively an easy and certain operation.

The aspect of steel when so broken as to exhibit a clean fracture, varies from an uniform silky and even surface of an almost silvery whiteness, to a fine or even coarse-grained texture, of a more blue or iron-like aspect; the finer-grained varieties are generally preferred, but no very important or at least unerring conclusions respecting its quality can be

drawn either from texture or colour. The microscope, however, enables us to observe some remarkable peculiarities in steel, not only in its varying texture as it comes from the manufacturer, but also before and after hardening. The fact of its diminution of density after hardening, or in other words, the increase of bulk which it then sustains, has long been known. Steel, of the specific gravity of 7·738, was found by Hawksbee to be thus reduced to 7·704. Brisson found the density of good English steel to be increased by hammering from 7·833 to 7·872. After hardening, the former had decreased to 7·816, and the latter to 7·818. Dr. Thomson found the density of good blistered-steel to be 7·823; when heated to redness and suddenly plunged into cold water its density was reduced to 7·747. The specific gravity of a piece of cast-steel he found = 7·8227; but when hardened only = 7·7532. (*Inorg. Chem.*, i. 497.) I have found even greater differences; and, in fact, the higher the heat to which the steel is raised, and the colder the medium in which it is cooled, the greater will be the resulting difference of density; for it is probable that the increased bulk attained by the steel under the expansive influence of heat, is retained by the suddenly cooled mass, and hence the peculiar state of tension into which it must be thrown when it has ultimately cooled down to the temperature of the atmosphere; and, indeed, it is surprising that masses of steel, which have undergone the process of hardening, are not more brittle and uncertain than experience proves them to be.

The quality of steel is sometimes tested by washing over its clean surface with dilute nitric acid, which ought to produce an uniform gray or blackish colour: if the steel is imperfect, and contains veins or pins of iron, they become evident by their difference of colour. When some particular kinds of iron or steel are thus tested, a mottled appearance is produced, as if it were composed of layers or wires of iron and steel welded together: hence is supposed to arise the peculiar character of the celebrated *Damascus* sword-blades.

ALLOYS OF STEEL.—Attempts have been made to improve the quality of steel by alloying it with some other metals, but none of these combinations have been found, after due experience, to be superior to the best ordinary steel. We shall again have occasion to notice them; but for details upon this subject, the reader is referred to the papers of Messrs. Stodart and Faraday, already quoted (*Quart. Jour.*, ix. 319), and to the volume of LARDNER'S *Cyclopædia*, treating on iron and steel.

§ X. ZINC.

ZINC, or *Spelter*, as it is sometimes called in commerce, is found in the state of oxide and of sulphuret. The metal zinc is first mentioned by Paracelsus, but the use of its ores, in converting copper into brass, was probably known to the ancients. In China and India zinc is said to have been known from time immemorial, and various utensils of zinc, sometimes inlaid and ornamented with other metals, are common in those countries. Perfectly-pure zinc is very difficultly obtained; it may be procured in a state approaching to extreme purity by dissolving the purest kinds of zinc that occur in commerce in dilute

sulphuric acid, and immersing a plate of zinc for some hours in the solution, which is then filtered, decomposed by carbonate of potassa, and the precipitate, after having been welledulcorated, heated with charcoal in an iron or earthen retort in a proper furnace. The zinc being volatile at a white-heat may thus be distilled over into water, care being taken that the neck of the retort is short and wide, otherwise it will be stopped up by the condensed metal. The common zinc of commerce generally contains a portion of lead, copper, iron, cadmium, traces of arsenic, sulphur, and manganese, and a little plumbago; these impurities chiefly remain in the form of a black powder when it is dissolved in dilute sulphuric acid, but the arsenic (and probably minute portions of some of the other metals) is carried off with the hydrogen.

Zinc is a bluish-white metal, with considerable lustre, rather hard, of a specific gravity of about 6·8 in its usual state; but, when drawn into wire, or rolled into plates, its density is augmented to 7 or 7·2. Its specific heat is 0·09555. (REGNAULT.) It has a peculiar odour when breathed upon or handled with moist fingers. In its ordinary state, at common temperatures, it is tough, and with difficulty broken by blows of the hammer. It becomes very brittle when its temperature approaches that of fusion, which is about 773°; but at a temperature a little above 212°, and between that and 300°, it becomes ductile and malleable, and may be rolled into thin leaves, and drawn into moderately fine wire, which, however, possesses but little tenacity. When a mass of zinc, which has been fused, is slowly cooled, its fracture exhibits a lamellar and prismatic crystalline texture. The equivalent of zinc is 32. (32·2 GMELIN, 32·3 TURNER, 32·31 GRAHAM.)

When a surface of clean and polished zinc, which may be made beautifully brilliant, is exposed to air and moisture at common temperatures, it soon tarnishes, and acquires a silvery-gray colour from superficial oxidizement: it then remains for a long time unchanged. It has lately, in consequence of its lightness and cheapness, been much used for roofing, gutters, and chimney-tops; but it should not, as is sometimes the case, be rivetted with copper nails, the contact of which with the zinc accelerates the decay of the latter by electric action.

ZINC AND OXYGEN.—The high attraction which exists between zinc and oxygen, is shown by the facility with which nearly all the other metallic oxides, when in solution, are reduced to the metallic state by its means. Its important electro-generative power in the Voltaic apparatus, is also referable to this cause. When zinc-filings are put into water, and air carefully excluded, they suffer little change; but if air be admitted, hydrogen is gradually evolved, and the metal becomes incrustated with a gray powder. The same product is obtained by long exposure of zinc to moist air, or by exposing the metal to the joint action of heat and air at a temperature just sufficient to fuse it. This is probably a mere mixture of metallic zinc and oxide of zinc: by some it is regarded as a true *sub-oxide* ($2Zn + O$), and a similar compound is obtained, according to Dulong, by decomposing oxalate of zinc at a red heat in a retort.

PROTOXIDE OF ZINC. ($Zn + O$) or ZnO .—This is the only salifiable oxide of zinc: it is obtained by intensely heating the metal exposed to air.

At a high red-heat (941° FAHR.) its vapour takes fire, and air being freely admitted, burns with a very bright flame, and is converted into a white flocculent tasteless substance, formerly called *nihil album*, *philosopher's wool*, and *flowers of zinc*. When this combustion goes on with violence, the oxide, though in itself not volatile, is carried up in flocculi by the current of air, which are so light as to remain for a long time floating about in the atmosphere. A piece of rolled zinc-leaf may also be inflamed by a spirit lamp, and will continue to burn brilliantly even when removed from the flame: if inflamed and plunged into a jar of oxygen gas, the combustion is as vivid as that of phosphorus; and indeed the splendour of the flame arises in both instances from the same cause, namely, the ignition of finely divided solid incombustible matter (see p. 224). The oxide of zinc, as prepared by combustion, generally contains small particles of the metal, which render it gritty, and require to be separated by washing; hence, for pharmaceutical use, it is best prepared by precipitating solution of sulphate of zinc by ammonia, and washing and drying the precipitate. It has been used as a pigment, both with oil and water; and is employed in medicine as a tonic, and as an external application. It is sometimes made upon a large scale, and is then seldom pure, being tainted by oxide of iron and other substances: the whiter parts of such oxide used to be called *pompholix*, and the gray, or less pure portions, *tutty*; and a patent has lately been taken for the employment of these and other impure oxides of zinc, as a substitute for white-lead in the manufacture of common oil paint, it appearing that they are equally capable of combining with, or producing a *body* as it is termed, when ground with linseed or other drying oil. If it be removed in large flakes from the crucible in which it is forming, and carried into a dark room, they continue for some time luminous.

Pure oxide of zinc is perfectly white; at a high temperature it acquires a tint of yellow, but again whitens as it cools. It is readily soluble in the acids; it also dissolves in the caustic fixed alkalis, and in pure and carbonated ammonia. The strong ammoniacal solution becomes turbid when dilute, and deposits its oxide when boiled. The solutions in potassa and soda yield a white deliquescent mass on evaporation: these, however, can scarcely be called chemical combinations. When a solution of alumina in caustic potassa is mixed with an ammoniacal solution of oxide of zinc, a definite combination of the earth and oxide is thrown down, containing, according to Berzelius, 6 proportionals of alumina and 1 of oxide of zinc, and being identical in composition with the mineral called *Gahnite*. The solutions of zinc decomposed by the alkalis furnish bulky white precipitates, consisting of *hydrated oxide*; this loses water at a red heat, and is then of the same composition as the oxide obtained by the rapid combustion of the metal. Thenard has described a *peroxide of zinc* obtained by agitating the hydrated oxide with oxygenated water: it is not a permanent compound, and forms no distinct salts with the acids. When zinc is subjected to the action of air and water, carbonic acid being excluded, it forms a hydrated oxide in acicular crystals, composed, according to Mitscherlich, of 3 atoms of zinc, 1 of oxygen, and 1 of water.

Protoxide of zinc consists of

				Proust.	Berzelius.	Döbereiner.
Zinc	1	32	80	80	80.1	81.64
Oxygen	1	8	20	20	19.9	19.36
Protoxide of zinc	1	40	100	100	100.0	100.00

It has been ascertained by A. de la Rive, that the energy with which zinc is acted on by dilute sulphuric acid is greatly dependent upon the purity of the metal; that when perfectly pure the action is comparatively feeble, but that when it contains minute portions of other metals, not exceeding (in regard to iron) a 1 to 200th part, the action becomes rapid: this is apparently owing to galvanic causes; and when a piece of pure zinc is wound round with platinum wire an equivalent effect is produced. De la Rive examined the action of dilute sulphuric acid, on pure zinc and on alloys of 9 parts of pure zinc with 1 of the several metals which are usually found in it, with the following results:—

	Gas evolved in a given time.
Zinc of commerce, and alloy of zinc and iron	100
Alloy of zinc and copper	43
„ zinc and lead	15
„ zinc and tin	12
Distilled zinc	5

A mixture of 100 parts of water with from 33 to 50 of sulphuric acid is that which acts most intensely on the metal.

Dumas observes that the commercial oxide of zinc is sometimes adulterated with starch, chalk, carbonate of magnesia, or alumina. Starch is detected by iodine; alumina may be separated by acetic acid, which dissolves the oxide of zinc; when the solution has been precipitated by a hydrosulphuret, lime and magnesia may be detected by the usual tests. In medicine, oxide of zinc is employed as a tonic, but by long continued use it acts as a slow poison. (PEREIRA, *Mat. Med.*, 524.)

CHLORIDE OF ZINC ($Zn + Cl$) is formed by heating leaf-zinc in chlorine, or by evaporating a solution of zinc in hydrochloric acid to dryness, and heating the residue red-hot in a glass tube. It is also obtained by distilling a mixture of zinc-filings and corrosive sublimate, or a mixture of dried sulphate of zinc and chloride of sodium. It is a white semi-transparent substance, fusible at about 212° , and volatile at a red heat. It has a nauseous styptic taste and is powerfully emetic. It is used in surgery as a caustic; and in medicine, in very minute doses, as a tonic. It was formerly called *butter of zinc*. It is readily soluble in water, and the solution gives on evaporation a very difficultly crystallizable and extremely deliquescent salt, generally called *muriate of zinc*, and which, when heated in the open air, partly-sublimes in the form of chloride, and is partly resolved into hydrochloric acid and oxide of zinc, in consequence of the presence of water. Its concentrated solution deposits oxide of zinc upon the addition of water, and the diluted solution dissolves the oxide when concentrated by evaporation. The solution of chloride of zinc is always slightly acid, and the addition of ammonia does not render it neutral till all the oxide is precipitated. The attraction of zinc for chlorine is so great, that it is often employed for separating chlorine from other combinations. Chloride of zinc consists of

				J. Davy.	
Zinc	1	32	47	50	
Chlorine . . .	1	36	53	50	
Chloride of zinc	1	68	100	100	

CHLORATE OF ZINC ($Zn + Cl$) crystallizes in octoëdra, and is a very soluble salt. It is best obtained by dissolving carbonate of zinc in chloric acid. When metallic zinc is digested in chloric acid, a portion of chloride of zinc is formed. (VAUQUELIN, *Ann. de Ch.*, xcv. 116.)

IODIDE OF ZINC. ($Zn + i$).—Iodine and zinc exert a powerful mutual affinity: the iodide is easily obtained by adding iodine to zinc-filings in water and applying a gentle heat: the iodine is added till it begins to discolour the solution; in excess, it is dissolved by the iodide which is formed. On evaporating the solution to dryness in a retort, the remaining iodide of zinc may be fused, and at a higher temperature it rises in vapour and condenses in prismatic crystals. Heated in the open air, iodine goes off and oxide of zinc is formed: its aqueous solution is also decomposed by exposure to air with the separation of iodine and the formation of oxide. It consists of

				Gay Lussac.	
Zinc	1	32	20.4	20.48	
Iodine	1	126	79.6	79.52	
Iodide of zinc	1	158	100.0	100.00	

IODATE OF ZINC. ($Zn + i'$).—When a soluble iodate is added to a solution of sulphate of zinc, it forms a difficultly-soluble iodate of zinc, which gradually falls in spherical grains. The salt may also be formed by dissolving recently precipitated oxide or carbonate of zinc in iodic acid. (GAY LUSSAC, *Ann. de Ch.*, xci. 85.)

BROMIDE OF ZINC ($Zn + b$) is formed either by passing bromine vapour over heated zinc; or by agitating a mixture of zinc, bromine, and water: a colourless solution results, which, when evaporated to a pellicle, crystallizes on cooling. Bromide of zinc has a sweetish astringent taste; is very deliquescent; fuses at a red heat, and at a higher temperature sublimes in white vapour: it is soluble in alcohol, ether, in acetic and hydrochloric acids, and in ammonia. (DUMAS.) It consists of

Zinc	1	32	29.2
Bromine . . .	1	78	70.8
Bromide of zinc	1	110	100.0

FLUORIDE OF ZINC is very difficultly soluble: with fluoride of potassium it forms a more soluble triple salt. (BERZELIUS.)

NITRATE OF ZINC is a deliquescent salt, which crystallizes with difficulty in four-sided prisms terminated by four-sided pyramids. They are copiously soluble in water and alcohol; when thrown upon glowing coals they are decomposed, and give to flame a bluish-green colour. The action of strong nitric acid upon zinc is so intense, as sometimes it is said to produce ignition; during the decomposition, nitrous and nitric oxide, and ultimately nitrogen, are evolved, and some ammonia is formed. The crystals of nitrate of zinc contain about 36 per cent. of water; they are therefore constituted of

Oxide of zinc	1	40	27.0
Nitric acid	1	54	36.5
Water	6	54	36.5
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Crystallized nitrate of zinc	1	148	100.0

SULPHURET OF ZINC ($Zn + S$) exists native under the name of *Blende*. It may be formed artificially by heating oxide of zinc with excess of sulphur, and is then of a yellow-brown colour. It is also produced by heating rapidly and suddenly a mixture of zinc-filings and sulphuret of mercury: the mercury is revived, and intense action ensues during the union of the zinc and sulphur. By passing the vapour of sulphur over fused zinc, Mr. E. Davy obtained a white crystalline substance resembling native phosphorescent blende. When a salt of zinc is precipitated by hydrosulphuret of potassa, a white compound is obtained, composed, according to Berzelius, of 72 oxide of zinc, 25 sulphuretted hydrogen, 3 water. It is probably a monohydrated sulphuret of zinc. Berthier formed a yellow crystalline sulphuret of zinc by heating anhydrous sulphate of zinc white-hot for an hour in a crucible lined with charcoal. It is observed by Dumas, that considering the strong affinity of zinc for oxygen and chlorine, its feeble affinity for sulphur is remarkable. Hydrogen and charcoal decompose blende at a white heat; in the former case sulphuretted hydrogen, and in the latter, sulphuret of carbon is formed. Sulphuret of zinc, native or artificial, consists of

				Arfwedson.
Zinc	1	32	66.7	66.34
Sulphur	1	16	33.3	33.66
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Sulphuret of zinc	1	48	100.0	100.00

OXYSULPHURET OF ZINC.—When hydrogen is passed over sulphate of zinc at a high temperature, a pulverulent residue is obtained, composed of 1 atom of oxide and 1 of sulphuret of zinc. Karsten analyzed some hexagonal crystals which lined one of the zinc-furnaces at Freiburg, and found them composed of 4 atoms of sulphuret and 1 atom of oxide of zinc. (DUMAS.)

Native Sulphuret of Zinc. *Blende* occurs in crystals which are brittle, soft, and of different shades of brown and black. Its primitive form is the rhomboidal dodecaëdron. It usually contains traces of iron and lead. It is an abundant mineral, and important as a source of the pure metal, which is obtained by roasting the ore, and afterwards exposing it to heat in proper distillatory vessels, mixed with charcoal. The English miners call it *black jack*.

HYPOSULPHITE OF ZINC ($Zn + \frac{1}{2}S$) was obtained long ago by Fourcroy, who considered it as a *sulphuretted sulphite*: he formed it by digesting metallic zinc in sulphurous acid, sulphuretted hydrogen is disengaged, and by gentle evaporation crystals are obtained, which are to be digested in alcohol; this liquid dissolves the hyposulphite, and affords it in prismatic crystals. A mixture of oxide of zinc and sulphur treated by sulphurous acid, affords the same salt; it is efflorescent, and easily decomposed by heat. (FOURCROY, *Système des Connoissances Chimiques*, v. 380.)

SULPHITE OF ZINC ($Zn + \frac{1}{2}S$) is easily formed by dissolving the oxide in sulphurous acid; it is more easily crystallizable and much less soluble in water than the hyposulphite, and is insoluble in alcohol.

HYPOSULPHATE OF ZINC ($\text{Zn} + \text{S}'$) is obtained by adding a solution of hyposulphate of baryta to sulphate of zinc; it is very soluble, and difficultly crystallizable. The crystals are composed of

Oxide of zinc	1	40	24.1	Heeren. 24.25
Hyposulphuric acid	1	72	43.4	43.51
Water	6	54	32.5	32.24
Crystals of hyposulphate of zinc	1	166	100.0	100.00

SULPHATE OF ZINC. ($\text{Zn} + \text{S}'$).—Zinc is readily oxidized and dissolved by dilute sulphuric acid, and hydrogen gas is given off: the zinc decomposes the water of the acid (according to Graham), that is, the *sulphate of water*; so that in fact an atom of zinc is substituted for an atom of hydrogen: thus we begin with $(h + o) + (s + 3o) + zn$, and end with $(zn + o) + (s + 3o) + h$. A transparent colourless solution of *sulphate of zinc* results, which by evaporation affords crystals in the form of four-sided prisms, terminated by four-sided pyramids. They have been described by Brooke (*Ann. of Phil., N.S.*, vi. 437). This salt effloresces slightly in a dry air; it is usually stated to be soluble in 2.5 parts of water at 60° ; but, according to Dumas, at that temperature 100 parts of water dissolve 140 of the salt: the very dense solution is used, he says, in hydrostatic lamps. When sulphate of zinc is heated, it fuses and gradually gives out its water of crystallization; at a red heat its acid begins to pass off, and at a very high temperature it is entirely decomposed, leaving oxide of zinc. It consists, in its anhydrous state, of

			Tennant.	Wenzel:
Oxide of zinc	1	40	50	46.19
Sulphuric acid	1	40	50	53.81
Sulphate of zinc	1	80	100	100.00

The ordinary crystals are constituted of

			Mitscherlich.
Anhydrous sulphate of zinc	1	80	56
Water	7	63	44
Crystals of sulphate of zinc	1	143	100
			100.00

The crystals formed at a temperature exceeding 36° , contain 6 equivalents of water, and are in the form of an oblique rhombic prism. (MITSCHERLICH.) When sulphuric acid is added to a concentrated solution of sulphate of zinc, a white pulverulent sulphate falls, containing 2 equivalents of water. (KUHN.)

The *white vitriol*, or sulphate of zinc of commerce, is often obtained by the oxidizement of blende, and is therefore very impure; it generally contains a subsulphate of zinc, together with the sulphates of iron, copper, cadmium, alumina, and sometimes lead.

Native Sulphate of Zinc occurs at Holywell in Flintshire, and in other places where the sulphuret of zinc is found; it is probably the result of the decomposition of that ore, and is often contained in the waters of the mines.

TRIS-SULPHATE OF ZINC. ($3\text{Zn} + \text{S}'$).—When oxide of zinc is boiled in a solution of sulphate of zinc, or when the salt is partially decomposed by potassa, and the precipitate which falls boiled in water, a salt is formed

which crystallizes in opaque shining scales, composed, according to Vogel, of 3 atoms of oxide of zinc and 1 of sulphuric acid.

AMMONIO-SULPHATE OF ZINC is obtained, according to Thomson, by mixing solutions of the two constituent salts in atomic proportions, and concentrating by evaporation. It crystallizes in white rhomboids, which readily dissolve in water, and consist of 1 equivalent of each of the sulphates, and 7 of water. Anhydrous sulphate of zinc greedily absorbs ammonia, 100 parts taking up 53·7 of the dry gas, and producing much heat. (H. ROSE, *Ann. de Ch. et Ph.*, Lxii. 311.)

SULPHATE OF ZINC AND POTASSA forms flat rhomboidal crystals, permanent in the air, and soluble in 5 parts of water at 60°. (H. STOKES, *Phil. Mag.*, 2nd series, ii. 428.) They consist of 1 equivalent of each of the sulphates and 7 of water.

PHOSPHURET OF ZINC is a brilliant lead-coloured compound, formed by distilling in a coated retort a mixture of 2 parts of zinc, and 1 of phosphorus.

Neither *Hypophosphite* nor *Phosphite of Zinc* have been examined.

PHOSPHATE OF ZINC is not crystallizable. It may be obtained by dissolving zinc in phosphoric acid, and evaporating to dryness. A phosphate of zinc is also precipitated upon the addition of phosphate of soda to sulphate of zinc. These salts have not been precisely examined, but it is probable there is a *subphosphate*, a *phosphate*, and a *biphosphate* of zinc. According to Graham, the minute crystals which fall when dilute solutions of phosphate of soda (rhombic) and sulphate of zinc are mixed, are a phosphate of zinc with an atom and a half of water, or they may be represented by the formula, $2(zn + o) + (h + o) + 2(p + \frac{1}{2}o) + 2(h + o)$.

CARBONATE OF ZINC ($Zn + car'$) may be formed by passing carbonic acid through water containing diffused hydrated oxide of zinc. The precipitate formed by adding carbonate of potassa to sulphate of zinc, is, according to Berzelius, a mixture of carbonate and hydrated oxide, analogous to the *magnesia alba*. Some of the varieties of *calamine* appear to consist of anhydrous carbonate of zinc. Specimens from Somersetshire and Derbyshire yielded

						Smithson.
Oxide of zinc	. 1	. . 40	. . 64·5	. . 65		
Carbonic acid	. 1	. . 22	. . 35·5	. . 35		
	1	62	100·0	100		

Another variety of calamine, from Bleiberg, in Carinthia, is probably a hydrous subcarbonate, consisting of

						Smithson.
Oxide of zinc	. 3	. . 120	. . 71	. . 71·4		
Carbonic acid	. 1	. . 22	. . 13	. . 13·5		
Water	. . . 3	. . 27	. . 16	. . 15·1		
	1	169	100	100·0		

Calamine occurs both crystallized and massive; its primitive form is an obtuse rhomboid. It is often found investing carbonate of lime, which has sometimes been decomposed, and the calamine remains in pseudo-crystals. It abounds in Somersetshire, Flintshire, and Derbyshire. A beautiful variety, coloured by carbonate of copper, is found at Matlock.

The variety of calamine, known by the name of *electric calamine*, from its property of becoming electrical when gently heated, consists of oxide of zinc in combination with silica.

REDUCTION OF THE ORES OF ZINC.—The zinc of commerce is procured from the native sulphuret, and from calamine, by the following process. The ore is first picked and broken into small pieces, and then submitted to a dull red-heat in a reverberatory furnace, by which carbonic acid is driven off from the calamine, and sulphur from the blende. It is then washed, ground, and thoroughly mixed with about one-eighth its weight of powdered charcoal. This mixture is put into large earthen pots, not unlike oil-jars, six of which are usually placed in a circular furnace; each pot has an iron tube passing from its lower part, through the floor of the furnace, and dipping into water; they are everywhere else firmly luted: upon the application of a red-heat, the metal distils through the tube into the water beneath, whence it is collected, melted, and cast into cakes. The details of the process for the reduction of zinc will be found in URE's *Dict. of Arts and Manufactures*, and in DUMAS' *Chim. app. aux Arts*.

BORATE OF ZINC is an insoluble white powder.

CYANURET OF ZINC ($zn + cy$) forms an insoluble white powder, when solution of cyanuret of potassium is added to sulphate of zinc; or when hydrocyanic acid is added to acetate of zinc; it is insoluble in alcohol, but soluble in ammonia, and in dilute hydrochloric acid with the separation of hydrocyanic acid. It consists of

Zinc	1	32	55.2
Cyanogen . . .	1	26	44.8
<hr/>					
Cyanuret of zinc	1	58	100.0

By destructive distillation in a retort, it leaves a black *carburet of zinc*.

FERROCYANURET OF ZINC is thrown down in the form of a white gelatinous precipitate, when hydroferrocyanic acid is added to a soluble zinc-salt.

ZINCOCYANURET OF POTASSIUM.—When cyanuret of zinc is dissolved in a solution of cyanuret of potassium, filtered, and evaporated, large octoëdral crystals are obtained, anhydrous, decrepitating when heated, and then fusing into a transparent colourless liquid. (L. GMELIN.)

FERROCYANURET OF ZINC AND POTASSIUM.—When a solution of ferrocyanuret of potassium is added to a zinc-salt, the white precipitate which falls is not a ferrocyanuret of zinc, but a double ferrocyanuret. It is represented by the formula ($^3zn + po + ^2fey$). When dried in the air it retains 12 atoms of water. (MOSANDER.)

ALLOYS OF ZINC.—With *potassium* and *sodium*, zinc forms brittle alloys, decomposable by exposure to air and water. Its alloy with *manganese* is unknown. With *iron* it yields a white and somewhat malleable alloy, which is difficult to form; but if plates of hot iron be dipped into melted zinc, they acquire the appearance of tin-plate, for which they are a most valuable substitute, inasmuch as the zinc-coated iron is prevented from oxidizement and rusting by the electrical relations of the metals: the zinc it is true is more subject to oxidizement, but so long as any of it remains

the iron is protected; and, when covered by a coat of paint, is extremely durable. Hurdles, fences, and all out of door iron-work, as well as locks, bolts, hinges, and other implements used in damp situations, and all iron-work employed in the contact of water, may be thus defended. It is to be regretted that the patent obtained some years ago for this manufacture has never been brought into active operation.

CHARACTERS OF THE SALTS OF ZINC.—They are mostly soluble in water, and the solutions are colourless, and have a peculiarly unpleasant astringent and metallic taste: they are not precipitated by iodide of potassium. Potassa, soda, and ammonia, form white precipitates, soluble in excess of the alkali, and in dilute sulphuric acid. In this case the precipitate is distinguished from alumina by its solubility in excess of ammonia. The precipitate formed in solutions of zinc by the carbonates of potassa and soda is not soluble in excess of those carbonates, but when carbonate of ammonia is used the precipitate is again dissolved. Sulphuretted hydrogen throws down a white hydrated sulphuret of zinc in perfectly neutral solutions, but not in those which are acid or alkaline. Hydrosulphuret of ammonia produces a white or yellowish-white precipitate. The soluble phosphates, carbonates, and borates, produce white precipitates soluble in acids and alkalis. Infusion of galls occasions no precipitate. The salts which are insoluble in water dissolve in dilute sulphuric acid, and are precipitated by ammonia, but generally dissolve in excess of acid or of precipitant. Metallic zinc is not thrown down from its solutions, by any of the other metals.

Before the blowpipe *oxide of zinc* becomes yellow when heated, but whitens as it cools. A small proportion forms with microcosmic salt and with borax a clear glass, which becomes opaque on increasing the quantity of oxide. A drop of nitrate of cobalt being added to the oxide, and dried and ignited, it becomes green. With soda, in the interior flame oxide of zinc is reduced, and the metal burns with its characteristic flame, depositing its oxide upon the charcoal. By this process zinc may be easily detected, even in the *automalite*. Mixed with oxide of copper, and reduced, the zinc will be fixed, and brass obtained. But one of the most unequivocal characters of the oxide of zinc is, to dissolve it in acetic acid, evaporate the solution to dryness, and expose it to the flame of a lamp, when the metal is reduced and burns with its peculiar flame.

§ XL. TIN.

TIN (Jupiter γ of the alchemists) has been known from the remotest ages. It was in common use in the time of Moses, and was obtained at a very early period from Spain and Britain by the Phœnicians. (PLINY, lib. iv. cap. 34, and xxxiv. cap. 47.) It occurs most abundantly in Cornwall; and is also found in Germany, Bohemia, and Hungary, in Europe; in Chili and Mexico; in the Peninsula of Malacca; and in India, in the Island of Banca. A little tin has also been found at Fahlun and Utö, in Sweden. Several varieties of tin occur in commerce, respecting which Vauquelin has given an useful essay. (*Ann. de Ch.*, lxxvii.) The *native oxide* is the principal *ore of tin*: the metal is obtained by heating it to redness with charcoal or culm, and a little lime; the first product is

impure and is returned into the furnace, and carefully heated so as to fuse the tin, which runs off into an iron kettle, while the principal impurities remain unmelted; in the kettle the tin is kept in fusion, stirred, and agitated by plunging wet charcoal into it, by which a quantity of impurities collect upon the surface, and are removed by a skimmer; thus refined, the metal is cast into blocks of about 3 cwt. each. The common ores are known under the name of *mine-tin*, and furnish a less pure metal than that obtained from *stream-tin*. The ordinary processes of reduction are described at length in AIKIN'S *Dictionary* (ART. TIN); by M. BONNARD (*Journ. des Mines*, xiv.); and by Mr. TAYLOR, in the 5th volume of the *Geological Transactions*. The purest kind of tin is known in commerce under the name of *grain tin*, a term formerly applied exclusively to the metal obtained from the stream-ore: *block-tin* is less pure, and is the produce of the common ore of the veins. The peculiar columnar fracture which pure or grain tin exhibits when broken, is given it by heating the mass till it becomes brittle, and then letting it fall upon a hard pavement from a height.

Tin has a silvery-white colour with a slight tint of yellow, and when so viewed as to exclude the white light reflected from its surface, it is decidedly yellow; it is malleable, though sparingly ductile. Common tin-foil, which is obtained by beating out the metal, is not more than 1-1000th of an inch in thickness, and what is termed *white Dutch metal* is in much thinner leaves.

Its specific gravity fluctuates from 7.28 to 7.6, the lightest being the purest metal. Its specific heat is 0.05623. (REGNAULT.) When bent it occasions a peculiar crackling noise, arising from the destruction of cohesion among its particles, and hence the brittleness and want of tenacity of tin-wire. When a bar of tin is rapidly bent backwards and forwards several times successively, it becomes so hot that it cannot be held in the hand. When rubbed it exhales a peculiar odour. It melts at 442°, and, by exposure to heat and air, is gradually converted into protoxide; but if the heat be continued till metallic tin no longer remains, the protoxide passes into peroxide. Placed upon ignited charcoal, under a current of oxygen gas, it enters into rapid combustion, forming the peroxide; and if an intensely-heated globule of the metal be thrown upon a sheet of dark-coloured paper, it subdivides into small particles, which burn very brilliantly, and leave lines of white oxide. It volatilizes at a very high temperature. When a polished surface of tin is heated it becomes yellow and iridescent, in consequence of superficial oxidization.

A preparation, under the name of *powdered tin*, is sometimes directed to be made for pharmaceutical use, by shaking the melted metal in a wooden box rubbed with chalk on the inside: *tin-filings* have also a place in some *Pharmacopœiæ*, and have been used as a vermifuge. These preparations are, however, both dangerous, the metal being rendered poisonous in the former case by slight oxidation, (ORFILA, *Traité des Poisons*, tom. i. 2me partie, p. 18,) and often creating very dangerous irritation when given in filings. The equivalent of tin may be assumed as 58. (57.9 TURNER, 59 GMELIN, 58.92 GRAHAM.) Its symbol is *sta* or Sn.

PROTOXIDE OF TIN. STANNOUS OXIDE. (*sta + o*) or STA, is obtained by precipitating a solution of protochloride of tin by ammonia; it falls in

the state of *hydrate*; when dried, out of the contact of air, it is of a dark colour, and undecomposable alone by heat. According to Cassola, protoxide of tin is formed by pouring nitric acid diluted with ten times its volume of water upon tin filings, and leaving them in contact 48 hours. When protochloride of tin is decomposed by a carbonated alkali, and the precipitate carefully dried at a temperature below 212° , it is also a *hydrated protoxide*, retaining no trace of carbonic acid.

Anhydrous protoxide of tin is best obtained by heating the hydrate to redness in a retort filled with carbonic acid; or by heating it in a glass-tube, and passing a current of dry carbonic acid over it till the water is carried off, and suffering it to cool out of the contact of air. The specific gravity of this oxide is 6.6. It is in the form of a black powder, which burns like tinder, on the contact of a red-hot wire, into peroxide. In the hydrated state it dissolves very readily in sulphuric, hydrochloric, and dilute nitric acids, and in caustic potassa and soda, but not in ammonia, nor in the alkaline carbonates. Its alkaline solution, when long kept, deposits metallic tin in arborescent crystals, and becomes a solution of the peroxide. The presence of protoxide of tin in solution is announced by its action on chloride of gold, with which it forms a purple precipitate. Protoxide of tin consists of

				Berzelius.	Proust.	Gay Lussac.
Tin	1	58	87.9	88.028	87	88.1
Oxygen . . .	1	8	12.1	11.972	13	11.9
Protoxide of tin	1	66	100.0	100.000	100	100.0

SESQUIOXIDE OF TIN. DEUTOXIDE OF TIN. ($sta + 1\frac{1}{2}o$).—When a saturated neutral solution of peroxide of tin in hydrochloric acid is mixed with moist hydrated peroxide of iron, an interchange of elements takes place, by which chloride of iron and sesquioxide of tin are formed: its solubility in ammonia distinguishes it from protoxide; and its giving a purple precipitate with chloride of gold, from peroxide.

PEROXIDE OF TIN. STANNIC OXIDE, ($sta + 2o$) or STA' , is formed by treating the metal with nitric acid. In its most concentrated form the acid does not immediately act, but on the addition of a few drops of water violent effervescence ensues, much heat is evolved, together with nitric oxide and nitrous acid vapour, some nitrate of ammonia is also formed, and the peroxide of tin remains in the form of a white insoluble powder; it may be purified by washing it with boiling distilled water, and may then be dried at a dull red-heat. Peroxide of tin is also formed by projecting a sufficient quantity of nitre upon red-hot tin. Fused with glass, it forms *white enamel*; but alone, it is extremely infusible, and when it has been heated it is insoluble in acids. The substance called *Tin putty*, is an oxide of tin, formed by levigating the crusts of oxide that form upon the metal when kept for some time in fusion. It is probably a mixture of the protoxide and peroxide.

When a solution of bichloride of tin is decomposed by ammonia, or by an alkaline carbonate, a bulky gelatinous precipitate falls, which, when washed and carefully dried, resembles gum: it is a *hydrated peroxide*, and retains 1 atom of water. In this state it is soluble in the acids; dilute hydrochloric acid dissolves it abundantly; but if it be

boiled in water, and then again collected and dried, it is no longer perfectly soluble in hydrochloric acid, but forms with it a subsalt; on pouring off the excess of acid the residue may be dissolved in water, but when hydrochloric acid is added it is again thrown down. These peculiarities have been referred to changes in its state of hydration. If the hydrated peroxide obtained by the action of nitric acid on tin be heated to redness, it becomes insoluble in the acids unless previously ignited with potassa or soda. The compounds of peroxide of tin with bases have sometimes been called *stannates*. This oxide consists of

				John Davy.	Proust.	Gay Lussac.
Tin	1	58	78.4	78.34	78.4	78.6
Oxygen	2	16	1.6	21.66	21.6	21.4
Peroxide of tin	1	74	100.0	100.00	100.0	100.0

Native Peroxide of Tin is generally gray, brown, or black, and sometimes transparent or translucent. The specific gravity of the native oxide is 7: its primitive crystal is an obtuse octoëdron, of which the modifications are extremely numerous. (W. PHILLIPS, *Geol. Trans.*, ii.) In some of the valleys of Cornwall, tin is found in rounded nodules, of various sizes, mixed with pebbles and rounded fragments of rocks. To separate the tin from the alluvial matter, currents of water are passed over it, and hence these deposits have been called *stream-works*, and the tin ore, *stream-tin*. One of the most extensive of these is a branch of Falmouth Harbour. A modification of stream-tin is called *wood tin*. It usually appears in small banded fragments of globular masses. The native peroxide of tin is insoluble in the acids, but if it be fused with potassa, the resulting stannate of potassa is soluble in water, and from it the soluble hydrated peroxide may be thrown down by the acids. The following are analyses of native oxide of tin from several localities (DUMAS):—

	Cornwall.	Bohemia.	Mexico.	Finbo.	Wood tin.
Peroxide of tin . . .	99.00	99.5	95.0	93.6	91
Oxide of iron . . .	0.25	0.5	5.0	1.4	9
Oxide of manganese . .	0.00	0.0	0.0	0.8	0
Silica	0.75	0.0	0.0	0.0	0
Oxide of columbium . .	0.00	0.0	0.0	2.4	0
	100.00	100.0	100.0	98.2	100

PROTOCHLORIDE OF TIN. (*sta + c.*)—Anhydrous protochloride of tin is obtained by subjecting a mixture of equal weights of protochloride of mercury and of an amalgam of tin and mercury to distillation, in a retort gradually raised to a dull red-heat; or a mixture of 1 part of tin-filings and 5 of bichloride of mercury may be treated in the same way. When hydrochloric acid gas is passed over heated tin in a glass tube, the protochloride is also formed, and hydrogen gas is given off. When tin is dissolved in hydrochloric acid, the solution evaporated, and the dry residue carefully heated to incipient redness in a small tube retort so as to exclude the action of air, the protochloride of tin remains nearly pure. It is in the form of a gray solid, of a resinous lustre, fusible and volatile at a high heat. When its solution in a small quantity of water is evaporated, it yields either acicular or prismatic crystals, which include 3 atoms of water, and of which the greater part may be expelled at 212°. When

a large quantity of water is poured upon these crystals they are partly decomposed, hydrochloric acid is separated and a white powder is formed, which is an *oxichloride of tin*, its components being 1 atom of protoxide, 1 of protochloride, and 2 of water. (BERZELIUS.) The protochloride of tin, or *salt of tin* of commerce, is made by putting 1 part of granulated tin into a jar or deep basin upon a sand-heat, and pouring upon it 1 part of hydrochloric acid, so that it may be exposed to the joint action of the acid and air; after some hours 3 parts more of the acid are added, and the mixture stirred and digested till a saturated solution is obtained. During the process a very fetid hydrogen gas is given off, and the greater part of the tin is dissolved; when the clear liquor is poured off it is set aside to crystallize; the mother-liquors are again evaporated as long as they afford crystals, and the residue is afterwards employed for conversion into bichloride.

In consequence of the decomposition above mentioned, the aqueous solution of protochloride of tin is always turbid, but becomes clear on the addition of hydrochloric acid. This acid solution quickly absorbs oxygen, and if added to certain metallic solutions, revives or deoxidizes them. It decomposes and precipitates sulphur from sulphurous acid. It reduces the persalts of iron to protosalts, and converts arsenic acid into arsenious acid, and chromic acid into oxide of chrome. With a very weak solution of corrosive sublimate it forms a gray precipitate of metallic mercury. Added to a dilute solution of chloride of platinum it changes its colour to a deep blood-red. With solution of gold it produces a purple precipitate used in painting porcelain, and known under the name of *Purple of Cassius*. With infusion of cochineal it produces a purple precipitate; and it is much used to fix and change colours in the art of dyeing and calico-printing. The greater number of vegetable infusions are precipitated by it, in consequence of the insoluble compounds which it forms with the varieties of extractive matter. (On the preparation of this salt see BERARD, *Ann. de Chim.*, LXVIII. 78; and CHAUDET, *Ann. de Ch. et Ph.*, iii. 276.) Protochloride of tin consists of

				J. Davy.	
Tin	1	58	61.7	62.22	
Chlorine	1	36	38.3	37.78	
Protochloride of tin	1	94	100.0	100.00	

AMMONIO-PROTOCHLORIDE OF TIN.—When protochloride of tin and hydrochlorate of ammonia are mixed, they form a double salt which crystallizes in the anhydrous state and also with 3 equivalents of water. The anhydrous protochloride of tin also absorbs ammonia, 2 equivalents of the former combining with 1 of the latter. With chloride of potassium the protochloride of tin also forms a definite double-salt. (ARJOHN. PERSOZ.)

PERCHLORIDE OF TIN. (*sta + 2c.*)—If tin be heated in excess of chlorine, or if amalgam of tin be distilled with excess of bichloride of mercury, a *perchloride* is obtained. The best proportions are 6 parts of tin, previously combined with 1 of mercury, and intimately mixed with 30 of the bichloride of mercury. The mixture is put into a glass retort with a sufficiently capacious receiver luted to it, and may be distilled over a small charcoal fire. The heat should be slowly raised, to prevent

too sudden action. Towards the end of the process a little of the protochloride rises, which the old chemists, from its consistency and appearance, called *Butter of Tin*. Perchloride of tin may also be procured by distilling 8 ounces of finely-powdered tin with 24 of bichloride of mercury, or by passing chlorine over the protochloride of tin. It is a transparent colourless fluid, formerly called *Libavius's Fuming Liquor*: it exhales copious fumes when exposed to a moist air, and with one-third its weight of water it forms a crystallized hydrate. Its boiling-point is 250° ; and, according to Dumas, the density of its vapour is 9.19. It is instantly decomposed by metallic zinc, forming chloride of zinc and a precipitate of metallic tin.

A solution of perchloride of tin much used by dyers is made by dissolving tin in a mixture of 2 measures of hydrochloric acid, 1 of nitric acid, and 1 of water; or by exposing the protochloride to a gentle heat with a small addition of nitric acid. The dyers also prepare this solution by digesting tin-filings in single aquafortis, (nitric acid, sp. gr. 1.3,) to each pound of which, they add about 2 ounces of common salt or of sal-ammoniac: this compound acid takes up about one-eighth its weight of tin. These solutions are generally known under the names of *nitromuriate* or *oxymuriate of tin*. Bichloride of tin consists of

				J. Davy.	
Tin	1	58	44.6
Chlorine	2	72	55.4
Bichloride of tin	1		130		100.0

AMMONIO-BICHLORIDE OF TIN.—Ammonia is absorbed by anhydrous bichloride of tin; the compound forms a white powder which may be sublimed without decomposition, and is soluble in water: it is represented by the formula $(sta + 2c) + (n + 3h)$. (ROSE.) Perchloride of tin and hydrochlorate of ammonia also combine in single atomic proportions and form a salt which crystallizes in octoëdra, permanent in the air, and very soluble in water; their solution reddens litmus and becomes turbid when boiled; it converts the red of cochineal to a bright scarlet. (APJOHN.)

POTASSIO-BICHLORIDE OF TIN.—When solutions of chloride of potassium and bichloride of tin are mixed in single atomic proportions and evaporated, anhydrous octoëdral crystals are obtained, the formula of which is $(sta + 2c) + (po + c)$.

PROTIODIDE OF TIN. $(sta + i)$.—When equivalent proportions of solutions of iodide of potassium and protochloride of tin are mixed, a crystalline deposit of protiodide of tin ensues, of an orange-red colour, and sparingly soluble in cold water. When dissolved in boiling water, it is deposited on cooling in brilliant acicular groups. Exposed to air, this compound slightly deliquesces and forms peroxide of tin and hydriodic acid. It forms double salts with certain basic iodides, and in thus combining with the iodides of potassium, sodium, calcium, barium, and strontium, 2 atoms of the protiodide of tin unite to 1 of the basic iodide: but with hydriodate of ammonia it combines in single atomic proportions. (BOULLAY, *Ann. de Ch. et Ph.*, xxxiv. 372.) The protiodide of tin is composed of

Tin	1	58	31.5	Boullay. 32.01
Iodine	1	126	68.5	67.99
<hr/>				
Protiodide of tin	1	184	100.0	100.00

PERIODIDE OF TIN ($sta+2i$) is prepared by dissolving in hydriodic acid the hydrate of the peroxide precipitated by alkalis from the bichloride. It crystallizes in yellow crystals of a silky lustre, which are resolved by boiling water into hydriodic acid and peroxide of tin. (TURNER.)

Periodide of tin is also formed by passing the vapour of iodine over heated tin: it then forms a yellow fusible substance. When iodine, tinfilings, and water are mixed together, peroxide of tin and hydriodic acid are formed. Periodide of tin consists of

Tin	1	58	18.7
Iodine	2	252	81.3
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Periodide of tin	1	310	100.0

IODATE OF TIN has not been examined.

PROTOBROMIDE OF TIN ($sta+b$) is formed by dissolving tin in hydrobromic acid and evaporating to dryness. It resembles the protochloride of tin, and consists of

Tin	1	58	42.7
Bromine	1	78	57.3
<hr/>			
Protobromide of tin	1	136	100.0

PERBROMIDE OF TIN. ($sta+2b$).—Metallic tin and bromine act energetically on each other: the metal burns, and a white crystallized compound is obtained, readily fusible and volatile, yielding slight vapours in moist air, and dissolving in water. It consists of

Tin	1	58	27.1
Bromine	2	156	72.9
<hr/>			
Perbromide of tin	1	214	100.0

BROMATE OF TIN has not been examined.

FLUORIDE OF TIN is a soluble and crystallizable compound.

PROTONITRATE OF TIN may be formed by acting upon the metal by dilute nitric acid, or by dissolving the hydrated protoxide in dilute nitric acid; a yellow solution, which will not crystallize, is obtained; exposed to air it absorbs oxygen, and peroxide of tin precipitates, or according to Dumas, a hydrate of the protoxide. If evaporated, the oxide falls, and a portion of nitrate of ammonia remains. During the action of the dilute acid upon the tin no gas is evolved; it is therefore evident that water, as well as part of the acid, are here decomposed, and that the results may be thus represented:—

Atoms employed.		Atoms obtained.	
8 Tin	{ 8 tin }	8 nitrate of protoxide of tin	{ 8 tin
10 Nitric acid	{ 10 nitrogen }		{ 48 oxygen
3 Water	{ 53 oxygen }	1 nitrate of ammonia	{ 2 nitrogen
	{ 3 hydrogen }		{ 5 oxygen
			{ 3 hydrogen

Protonitrate of tin (assumed as anhydrous) consists of

Protoxide of tin	1	66	55
Nitric acid	1	54	45
Protonitrate of tin	1	120	100

PERNITRATE OF TIN.—The recently-precipitated peroxide of tin dissolves in nitric acid and forms a colourless solution, which has, I believe, furnished crystals. When diluted or heated, the solution becomes turbid; the addition of nitrate of ammonia renders this salt more stable, and probably forms with it a double salt. When strong nitric acid is made to act upon tin, as in the process above mentioned for the production of the peroxide, none of the metal is retained in solution, and on evaporation nitrate of ammonia only remains.

PROTOSULPHURET OF TIN. (*sta + s.*)—This compound may be procured by heating tin with sulphur; in consequence, however, of the high temperature required for its formation, so much of the sulphur is generally lost, that a mixture of the metal and of the sulphuret is only at first obtained. This mixture may be pulverized, and heated in a retort with its weight of sulphur, in which case the perfect protosulphuret is the result. A hydrated protosulphuret of tin is also precipitated, when the salts of the protoxide are mixed with solution of sulphuretted hydrogen, or with an alkaline protosulphuret. Obtained by the first process, it is a brittle blackish compound of a laminated texture, heavier than tin, fusible at a red heat, and occasionally forming acicular crystals; it dissolves in hydrochloric acid with the evolution of sulphuretted hydrogen. It consists of

J. Davy. Bergman.					
Tin	1	58	78.4	78.6	80
Sulphur	1	16	21.6	21.4	20
Protosulphuret of tin	1	74	100.0	100.0	100

SESQUISULPHURET OF TIN. (*sta + 1½ s.*)—Berzelius obtained this compound by heating the finely-powdered protosulphuret with one-third its weight of sulphur to dull-redness: it is of a yellowish-gray colour, metallic lustre, and when digested in hydrochloric acid gives out sulphuretted hydrogen, and leaves a yellow residue of bisulphuret. Gmelin regards this as a mixture of the protosulphuret and persulphuret. According to Berzelius it contains

Tin	1	58	70.6
Sulphur	1½	24	29.4
Sesquisulphuret of tin	1	82	100.0

BISULPHURET OF TIN. (*sta + 2 s.*)—It is frequently stated that this compound may be obtained by heating mixtures of sulphur and oxide of tin, but the result in these cases has probably been the preceding sesquisulphuret. A mixture of equal parts of tin-filings, sulphur, and sal-ammoniac, carefully heated in a covered crucible, yield a good bisulphuret of tin; sal-ammoniac, hydrosulphuret of ammonia, sulphuretted hydrogen, and sulphur, are evolved during the process. A mixture of equal parts of protosulphuret of tin, sal-ammoniac, and sulphur, yields the same results.

In these operations the sal-ammoniac is said to be indispensable, but according to Proust (NICHOLSON'S *Journal*, xiv. 39), when heat is gradually applied to a mixture of flowers of sulphur and protochloride of tin, "volatile fuming muriate will pass over in considerable quantity, the excess of sulphur will fix about the neck of the retort, and at the bottom will appear a light mass of brilliant mosaic gold, and part spangle the dome of the vessel with gold-coloured flowers." Woulfe has given several formulæ for the production of this sulphuret (*Phil. Trans.*, 1771); but the following, taken from the *London New Dispensatory* of 1765, answers best:—Take 12 oz. of tin and amalgamate it with 6 oz. of mercury, reduce it to powder, and mix it with 7 oz. of flowers of sulphur and 6 oz. of sal-ammoniac, and put the whole into a glass matrass placed in a sand heat. Apply a gentle heat till the white fumes abate, then raise the heat to redness, and keep it so for a due time. On cooling and breaking the matrass, the bisulphuret of tin is found at the bottom. (See Woulfe's Paper, and AIKIN'S *Dict.*, art. TIN.) According to Berzelius, the use of the mercury in these operations is to facilitate the fusion of the tin and its combination with the sulphur, while the sal-ammoniac prevents such increase of temperature as would reduce the tin to the state of protosulphuret.

A hydrated bisulphuret of tin is formed by decomposing a solution of perchloride of tin by sulphuretted hydrogen, avoiding the presence of excess of acid. The precipitate is pale yellow; it becomes of a dingy yellow when dried, and has a vitreous fracture.

The extraordinary golden lustre of the bisulphuret of tin and its flaky texture rendered it an object of great interest to the alchemists: it was termed *aurum musivum*, or *mosaic gold*. When well made it is in very soft golden flakes, very friable, and adhering to the fingers. It is insoluble in the acids, except in nitro-hydrochloric acid; it is soluble in caustic potassa, but not without partial decomposition. It is much used for ornamental work, under the name of *bronze-powder*, especially by the manufacturers of paper-hangings: it is chiefly imported from Holland and Germany. It consists of

			J. Davy.		Berzelius.
Tin	1	58	64.4	63.6	65
Sulphur	2	32	35.6	36.4	35
Bisulphuret of tin	1	90	100.0	100.0	100

HYPOSULPHITE OF TIN.—Tin decomposes an aqueous solution of sulphurous acid; sulphur is evolved, which forms sulphuret of tin: the oxide of tin formed, together with another portion of the sulphur and a certain quantity of sulphurous acid, unite and form a soluble hyposulphite which is retained in solution. (FOURCROY.)

SULPHITE OF TIN is formed by digesting the protoxide in sulphurous acid, but the salt has not been examined.

SULPHATES OF TIN.—When excess of tin is boiled in sulphuric acid, a solution is obtained which deposits white acicular crystals of *protosulphate of tin*. In this process sulphurous acid is evolved, and some sulphur generally set free, arising out of the simultaneous decomposition of the water and the acid; the nascent hydrogen and the sulphuric acid react on

each other, reproduce water, and deposit sulphur. Protosulphate of tin is also precipitated by pouring sulphuric acid into protochloride of tin.

When tin is boiled in excess of sulphuric acid, or when recently precipitated peroxide of tin is dissolved in the acid, a *persulphate of tin* is formed, which, however, cannot be brought to crystallize. Dumas observes, that these sulphates of tin probably form double salts with the alkaline sulphates.

PHOSPHURET OF TIN may be formed by dropping phosphorus into melted tin, or by heating to redness equal parts of tin-filings and superphosphate of lime, or phosphate of ammonia. It is of a silvery colour, sectile, and somewhat ductile. When its filings are sprinkled upon hot coals the phosphorus burns. Phosphuret of tin consists of

				Pelletier.
Tin	2	116	87	88
Phosphorus	1	16	13	12
Phosphuret of tin	1	132	100	100

PHOSPHITE OF TIN is produced, according to Rose, by mixing protochloride of tin with protochloride of phosphorus saturated by ammonia. (*Ann. de Ch. et Ph.*, xxxv. 218.)

PHOSPHATES OF TIN.—A *protophosphate* is formed by adding phosphate of soda to the protochloride. It is a white powder, not soluble in water, and fuses at a red heat into an opaque white enamel. The *perphosphate* of tin may also be formed by double decomposition: it resembles the protophosphate.

CARBONATE OF TIN.—When carbonate of potassa is added to protochloride of tin, a white precipitate ensues, which, when washed and dried, loses carbonic acid, so that no permanent carbonate appears to exist.

BORATE OF TIN is an insoluble white powder.

FERROCYANURET OF TIN.—Ferrocyanuret of potassium produces a white precipitate in solution of protochloride of tin.

ALLOYS OF TIN.—With *potassium* and with *sodium* tin forms brilliant white alloys, the latter being less fusible than tin. The potassium alloy is formed by heating a mixture of 100 parts of oxide of tin, 60 of calcined tartar, and 8 of lamp black. (SERULLAS.) Its alloys with the other light metals have not been examined, neither has that which it probably forms with *manganese*. With *iron* it forms combinations which are white, and more or less fusible according to the proportion of iron which they contain. These metals admit to a certain extent of separation by *liquation*; that is, when the alloys are heated up to a temperature short of their fusion the tin runs off, leaving a less fusible alloy, in which iron always predominates. Bergman observed, that on fusing tin and iron these metals had a tendency to form two definite alloys; the one containing 2 of tin and 1 of iron, the other, 2 of iron and 1 of tin.

Tin-plate is a most useful alloy of tin and iron, in which iron-plate is superficially alloyed with tin, and to the surface of which a quantity of tin further adheres, without being in combination. It is made by

dipping the cleansed iron-plates into a bath of melted tin; the process is described at length by Parkes. (*Chemical Essays*.) An alloy, composed of 6 parts of tin and 1 of iron, made by fusing tin with iron-turnings, is sometimes used as a substitute for pure tin in tinning copper vessels; its specific gravity is 7.247; it is brittle when hot, but somewhat malleable when cold; it fuses at a red heat. The objection to these combinations generally is, that in consequence of the electrical relations of the two metals, the iron, if anywhere exposed, has an increased tendency to rust and oxidizement. This is especially the case with tin-plate; for although the surface of the tin itself is sufficiently durable, no sooner is any portion so abraded as to denude the iron, than a spot of rust appears and rapidly extends; hence the superiority of iron-plate covered by zinc instead of tin, zinc being electro-positive, whereas tin is electro-negative in regard to iron.

Moiré metallique is merely tin-plate which has been superficially acted on by an acid so as to display by reflected light the crystalline texture of the tin; the tin-plate best suited for the purpose is that which has rather a thick coating of pure tin. It should first be well cleansed by washing its surface with a little caustic potash, then in water, and drying it. The acid employed is always some modification of the nitro-hydrochloric more or less diluted; 8 parts of water, 2 of nitric, and 3 of hydrochloric acid generally answers well. The plate should be slightly heated, and then quickly sponged over with the acid, so as to bring out the *moiré*; it should then immediately be dipped into water, well washed, and perfectly dried: if the acid has blackened or oxidized the surface, a solution of caustic potash will generally clean it. The crystals on the unprepared tin-plate are usually large and indistinct, so that its texture is often modified expressly for the purpose, by heating it up to the point of the fusion of the tin, powdering it over with sal-ammoniac to destroy the oxide, and then plunging it into cold water; in this way the crystals are generally very small. By sprinkling the surface of the heated plate with water, or by only partially fusing the tin by holding the plate over the flame of a spirit-lamp, or running the blowpipe flame over it, various modifications of the crystalline surface may be obtained, or different devices sketched as it were upon it. The plates are generally finished by a coating of transparent or coloured varnish.

Tin and zinc form a hard alloy, stronger than tin, and not brittle. An alloy of equal parts of zinc and tin resists friction, and is almost as tenacious as brass. (KOECHLIN.)

The *tinning of pins* is effected by boiling them for a few minutes in a solution of 1 part of bitartrate of potassa, 2 of alum, and 2 of common salt, in 10 or 12 of water, to which some tin-filings or finely granulated tin are added; they soon become coated with a brilliant and adhesive film of tin, and are then taken out, cleaned, and dried. The pins are made of brass wire, and require to be perfectly clean before they are put into the tinning liquor. (See the experiments of Gadolin and Gedda upon the precipitation of tin by copper. *Jour. de Phys.*, xxxiv. 362 and 430.)

Tin medals, or casts in tin, are *bronzed* by being first well cleaned, wiped, and washed over with a solution of 1 part of protosulphate of

iron, and 1 of sulphate of copper, in 20 of water: this gives a gray tint to the surface; they are then brushed over with a solution of 4 parts of verdigris in 11 of distilled vinegar; left for an hour to dry; and polished with a soft brush and colcothar.

CHARACTERS OF THE SALTS OF TIN.—The salts of the *protoxide* have a highly astringent and disagreeable taste; they are mostly colourless, and are precipitated white by ferrocyanuret of potassium, and brown by hydrosulphurets of the alkalis: white by caustic soda and potassa, and excess of alkali redissolves the precipitate. They reduce the persalts of many metals to the state of protosalts; such as the persalts of copper, iron, and mercury: with dilute solution of gold they give a red or purple precipitate. Succinates and benzoates of the alkalis give white, and tincture of galls yellow, precipitates. The salts of the *peroxide* are colourless, and do not reduce the other metallic persalts; heated with nitric acid, peroxide of tin is generally separated: they are precipitated white by ferrocyanuret of potassium, and dirty yellow by the hydrosulphuretted alkalis.

Protochloride of tin is decomposed by zinc and by cadmium, which quickly and entirely precipitate tin in a metallic state. Lead immersed in a solution of the protochloride of tin becomes covered with spicular crystals of the latter metal, which prevent further action. Pure and anhydrous perchloride of tin is not decomposed by any of the metals; if water be present it is acted upon as the protochloride. The alkaline solution of oxide of tin is reduced by zinc and cadmium, and less perfectly by lead.

§ XII. CADMIUM.

THIS metal was discovered in 1817, by the late Professor Stromeyer, of Göttingen, in examining into the cause of the yellow colour of certain oxides of zinc, which had been erroneously suspected to contain arsenic; he called it *Cadmium*, from *καδμεια*, a term formerly applied both to calamine, and to the substance which sublimes from the furnace during the manufacture of brass. It is contained in certain ores of zinc, and especially in the *black fibrous blende* of Bohemia. It has been detected by Dr. Clarke in the *calamine* of Derbyshire and Somersetshire, and in the zinc of commerce (*Ann. of Phil.*, xv. 272, and New Series, iii. 123), and Mr. Herapath found it in considerable proportion in the sublimate which, in the process for obtaining zinc, rises before that metal, forming what the workmen call the *brown blaze*. (*Ann. of Phil.*, iii. 435.)

Cadmium may be procured by digesting the ore in diluted hydrochloric acid, by which a mixed solution of chloride of zinc and cadmium is obtained: it should be evaporated to dryness, to drive off excess of acid, and re-dissolved in water. Immerse a plate of iron into this solution, to separate all that may be thus precipitated, and afterwards filter the liquor into a platinum capsule containing a piece of zinc. The cadmium will coat over the surface of the capsule, and adhere so firmly to it, that it may be washed, and thus freed from any remaining solution of zinc. Hydrochloric acid dissolves the precipitate with effervescence, and

from this solution it is thrown down white by the alkalis, and yellow by sulphuretted hydrogen. (WOLLASTON.) It may be reduced to the metallic state by mixing the oxide with charcoal, and applying a red heat in a tube or retort, when the cadmium, being volatile at that temperature, sublimes.

Stromeyer separates cadmium from the ores containing it, by digesting them in dilute sulphuric acid, and passing sulphuretted hydrogen through the acidulous solution. He washes the precipitate thus formed, dissolves it in hydrochloric acid, and expels the excess of acid by evaporation. He then redissolves the residue in water, precipitates by carbonate of ammonia, of which an excess is added, for the purpose of retaining the oxides of zinc and copper in solution; the remaining carbonate of cadmium is washed, dried, and heated with lamp-black, by which it is easily reduced.

Cadmium, in its physical properties, closely resembles tin, but it is rather harder and more tenacious; its specific gravity is 8.60, and somewhat exceeds 8.69 after hammering. It fuses at a temperature a little below that required by tin, and distils over at a heat somewhat below redness, condensing into metallic globules: its vapour is inodorous. Air does not act upon it except when heated, when it forms an orange-coloured oxide, not volatile, and easily reducible. Its equivalent is 56. (55.8 TURNER, 55.83 GRAHAM.)

PROTOXIDE OF CADMIUM. (*cad+o*) or CAD.—This, which is the only known oxide, may be obtained by burning the metal in oxygen, or by dissolving it in dilute nitric acid, and precipitating it in the state of carbonate, which is then washed, dried, and ignited. It is of a reddish-brown or orange colour, and is neither volatile nor fusible; but when mixed with carbonaceous matter it appears volatile, in consequence of its easy reduction, and the burning off of the separated cadmium. When thrown down from its solutions by alkalis it forms a white *hydrate*, soluble in excess of ammonia, but insoluble in potassa or soda.

Oxide of cadmium consists of

				Stromeyer.	John.
Cadmium	1	56	87.5	87.45	90
Oxygen	1	8	12.5	12.55	10
Protoxide of cadmium	1	64	100.0	100.00	100

CHLORIDE OF CADMIUM (*cad+c*) is formed by dissolving the hydrated oxide in hydrochloric acid: on evaporation small prismatic crystals are obtained, very soluble in water, and efflorescent in a dry atmosphere; they readily fuse, and losing water of crystallization, concrete into a transparent lamellar crystalline mass, which is *chloride of cadmium*: at a very high temperature it is volatile, and condenses in the form of a nacreous sublimate. It consists of

				Stromeyer.
Cadmium	1	56	60.9	61.38
Chlorine	1	36	39.1	38.62
Chloride of cadmium	1	92	100.0	100.00

IODIDE OF CADMIUM (*cad+i*) is a colourless crystallizable compound, fusible, and resolved at a high temperature into iodine and cadmium. It

is easily formed by heating filings of cadmium with iodine, or mixing them in a moist state. Its alcoholic or aqueous solution yields large six-sided tables, of a pearly lustre. It consists of

Cadmium	1	56	30.94	Stromeyer. 30.541
Iodine	1	126	69.06	69.459
Iodide of cadmium	1	182	100.00	100.000

BROMIDE OF CADMIUM.—Bromine does not act upon cadmium at common temperatures, but when the vapour of bromine is passed over cadmium highly heated in a tube, white vapours are formed, which afterwards condense. When bromine and filings of cadmium are mixed with water, a solution of bromide of cadmium is also obtained.

This compound is very soluble in water, and when its hot saturated solution cools, it deposits white acicular prisms, which effloresce in the air; when heated, these crystals fuse, lose water, and, at a red heat, sublime, yielding nacreous scales. This bromide dissolves in alcohol and ether, and in concentrated acetic and hydrochloric acid without decomposition; it is also very soluble in ammonia. (DUMAS.) It consists of

Cadmium	1	56	41.8
Bromine	1	78	58.2
Bromide of cadmium	1	134	100.0

FLUORIDE OF CADMIUM is a difficultly-soluble compound.

NITRATE OF CADMIUM ($\text{Cad} + n'$) forms radiated acicular crystals, which are deliquescent, and soluble in alcohol. They consist of

Oxide of cadmium	1	64	41.56	Stromeyer. 42.15
Nitric acid	1	54	35.06	35.78
Water	4	36	23.38	22.07
Crystallized nitrate of cadmium	1	154	100.00	100.00

SULPHURET OF CADMIUM ($\text{cad} + s$) is obtained in the form of a bright-yellow powder, insoluble in ammonia and in the fixed alkalis, by precipitating the solutions of the metal with sulphuretted hydrogen, or an alkaline sulphuret. It is also formed by heating cadmium, or its oxide, with sulphur, and concretes, on cooling, into a yellow lamellar mass. It dissolves with the evolution of sulphuretted hydrogen in concentrated hydrochloric acid, and is not volatile at a white heat. It furnishes a valuable yellow pigment, which mixes well with other colours. It consists of

Cadmium	1	56	77.78	Stromeyer. 78.02
Sulphur	1	16	22.22	21.98
Sulphuret of cadmium	1	72	100.00	100.00

HYPOSULPHATE OF CADMIUM is a very soluble deliquescent salt. (HEEREN.)

SULPHATE OF CADMIUM ($\text{Cad} + s'$) forms transparent prismatic crystals, much resembling those of sulphate of zinc: they are efflorescent, and very soluble in water: gently heated, they lose water of crystallization,

and at a higher temperature a part of the acid escapes, and a basic sulphate, difficultly soluble, and crystallizing in scales, remains. 100 parts of anhydrous sulphate of cadmium absorb 48·69 of ammonia, forming a bulky white powder. The crystals of sulphate of cadmium contain

	Stromeyer.			
Oxide of cadmium	1	64	45·72	45·956
Sulphuric acid	1	40	28·57	28·523
Water	4	36	25·71	25·521
Crystallized sulphate of cadmium	1	140	100·00	100·000

PHOSPHURET OF CADMIUM (*cad+p*) is a gray, brittle compound, with a feeble metallic lustre, and very difficult of fusion.

PHOSPHATE OF CADMIUM is an insoluble white powder, formed by adding neutral phosphate of soda to a soluble salt of cadmium. It consists, according to Stromeyer, of 69·2 oxide of cadmium, and 30·8 phosphoric acid: the equivalents would give 64+36. It fuses at a high heat into a transparent glass.

CARBONATE OF CADMIUM (*CAD+car'*) is a white insoluble anhydrous powder, which loses its acid at a red heat; and consists of

	Stromeyer.			
Oxide of cadmium	1	64	74·42	74·547
Carbonic acid	1	22	25·58	25·453
Carbonate of cadmium	1	86	100·00	100·000

BORATE OF CADMIUM is an insoluble white powder, containing, according to Stromeyer, 72·1 oxide, 27·9 acid; numbers which are irreconcilable with the equivalents.

ALLOYS OF CADMIUM.—Cadmium combines readily with other metals, forming brittle alloys, from which the cadmium is expelled by a high heat; few of them have been examined.

THE SALTS OF CADMIUM are white and colourless, and mostly soluble in water: the solution has a nauseous metallic taste; they are precipitated *white* by caustic and carbonated alkalis, and by ferrocyanuret of potassium; and *yellow* by sulphuretted hydrogen: they are not affected by tincture of galls. The precipitate by the carbonated alkalis is anhydrous, whereas, with solution of zinc, they throw down a hydrated carbonate; with carbonate of ammonia, the zinc salts give a precipitate soluble in excess of the precipitant; with cadmium salts the precipitate is insoluble. The yellow precipitate which sulphuretted hydrogen occasions in solutions of cadmium has sometimes been mistaken for sulphuret of arsenic; it differs in falling more promptly, in its easy solubility in concentrated hydrochloric acid, its insolubility in ammonia, and its fixity in the fire. Zinc is the only metal which throws down metallic cadmium. The scarcity of cadmium prevents its application to useful purposes, otherwise its malleability would render it available in the arts, and its oxide and sulphuret would perhaps be good pigments. Its applications in medicine would probably be analogous to those of zinc.

§ XIII. COBALT.

THE following account of the discovery of cobalt is given by Dr. Thomson. (*Inorg. Chem.*, i. 536.) "A mineral called *cobalt**, of a gray colour, and very heavy, has been used in different parts of Europe, since the fifteenth century, to tinge glass of a blue colour. But the nature of this mineral was altogether unknown till it was examined by Brandt, in 1733. This celebrated Swedish chemist obtained from it a new metal, to which he gave the name of *cobalt*. (*Acta Upsal.*, 1733 and 1742.) Lehmann published a very full account of everything relating to this metal in 1761. (*Cadmialogia, oder Geschichte des Farben-Kobolds.*) Bergman confirmed and extended the discovery of Brandt in different dissertations published in the year 1780. (*Opusc.*, ii. 444, 501, and iv. 371.) Scarcely any further addition was made to our knowledge of this metal till 1798, when a paper on it was published by Mr. Tassaert. (*Ann. de Chim.*, xxviii. 101.) In the year 1800, a new set of experiments were made upon it by the School of Mines at Paris, in order to procure it perfectly pure, and to ascertain its properties when in that state. (FOURCROY, *Discours Préliminaire*, p. 114.) In 1802, a new series of trials was published by Thenard, which throw considerable light on its combinations with oxygen. (*Ann. de Chim.*, xlii. 210.) And in 1806, Mr. Proust published a set of experiments upon the same subject. (*Ann. de Chim.*, ix. 260.) Considerable attention has been lately paid to the purification of this metal; but hitherto no one seems to have been fortunate enough to hit upon a method altogether free from objections."

The *native* combinations of cobalt are the oxide, and compounds of the metal with iron, nickel, arsenic, and sulphur. It is also found combined with arsenic acid. In the white and gray cobalt-ores, the metal is combined with iron, and with arsenic. The ore commonly called *glance cobalt*, from Tunaberg, in Sweden, is a sulpho-arseniuret of cobalt. Some of the varieties are crystallized in cubes, octoëdrons, and dodecaëdrons. The *red ore* is an arseniate. The finest specimens are the produce of

* The word *cobalt* seems to be derived from *Cobalus*, which was the name of a spirit that, according to the superstitious notions of the times, haunted mines, destroyed the labours of the miners, and often gave them a great deal of unnecessary trouble. The miners probably gave this name to the mineral out of joke, because it thwarted them as much as the supposed spirit, by exciting false hopes, and rendering their labour often fruitless; for as it was not known at first to what use the mineral could be applied, it was thrown aside as useless. It was once customary in Germany to introduce into the church-service a prayer that God would preserve miners and their works from *kobalts* and *spirits*. (See BECKMANN'S *History of Inventions*, ii. 362.) Mathesius, in his tenth sermon, where

he speaks of *cadmia fossilis* (probably cobalt ore), says, "Ye miners call it *cobalt*; the Germans call it the black devil and the old devil's whores and hags, old and black *kobel*, which by their witchcraft do injury to people and to their cattle." Lehmann, Paw, Delaval, and several other philosophers, have supposed that *smalt* (oxide of cobalt melted with glass and pounded) was known to the ancients, and used to tinge the beautiful blue glass still visible in some of their works; but we learn from Gmelin, who analyzed some of these pieces of glass, that they owe their *blue* colour, not to the presence of *cobalt*, but of *iron*. According to Lehmann, cobalt ore was first used to tinge glass blue by Christopher Schürer, a glassmaker at Platten, about the year 1540.

Saxony. Cobalt has also been detected, by Stromeyer, in several specimens of meteoric iron. Hydrated peroxide of cobalt is sometimes combined with native peroxide of manganese.

Cobalt is never employed in the metallic state, so that the processes for its reduction are generally carried on upon a small scale, and confined to the experimental laboratory.

To obtain pure cobalt, the cobalt of commerce, in fine powder, may be calcined with 4 parts of nitre, and washed in hot water, by which much arsenic is separated: then digest it in dilute nitric acid, and immerse a plate of iron into the solution, which will separate the copper; filter, and evaporate to dryness; digest the dry mass in liquid ammonia and filter; expel the excess of ammonia from the filtered liquor by heat, taking care not to produce a precipitate, and then add solution of potassa, which throws down oxide of nickel; filter immediately, and boil, which will occasion the separation of oxide of cobalt; this, ignited with charcoal, furnishes the pure metal. In this process the first calcination with nitre often requires two or three repetitions in order to get rid of the whole of the arsenic, which adheres to cobalt with much obstinacy.

When the ores of cobalt, or the impure oxide called *Zaffre*, are dissolved in hydrochloric acid by the aid of a little nitric acid, and sulphuretted hydrogen passed through the solution, the arsenic is precipitated: the filtered liquor may then be boiled with a little nitric acid to peroxidize the iron, and precipitated by carbonate of potassa: the precipitate, when well washed, is to be digested in oxalic acid, which leaves an insoluble oxalate of cobalt; this may be decomposed at a high heat. When dry hydrogen gas is passed over oxide of cobalt, it is also reduced.

The following is Liebig's process for obtaining a pure oxide of cobalt. The ore is pulverized and carefully torrefied; it is then projected by small portions at a time into a crucible or iron vessel, containing 3 parts of bisulphate of potassa, fused by a moderate heat: this mixture, at first fluid, soon acquires a thick pasty consistence; the fire is then raised till the mass is perfectly fused and white vapour no longer emitted. The fused mass is then taken out by an iron spoon, fresh bisulphate is put into the crucible, and fresh portions of ore treated as before. The fused mass contains sulphate of cobalt, neutral sulphate of potassa, perarseniate of iron, and a very little arseniate of cobalt. It is reduced to powder, and boiled (in an iron boiler) with water, to separate the soluble matters; the liquor is then filtered, or decanted, clear; it should be of a rose colour, and yields, with solution of carbonate of potassa, a precipitate of carbonate of cobalt. This is repeatedly washed with boiling water; the first waters hold sulphate of potassa in solution and may be evaporated to dryness and reconverted into bisulphate. This process is founded upon the permanence of sulphate of cobalt at a red heat, and the insolubility of the arseniates of iron and nickel in all neutral solutions. The oxide thus obtained is free from nickel, and should be so free from iron as not to be discoloured by infusion of galls: should it contain traces of copper they may be separated by sulphuretted hydrogen. The removal of arsenic from the fused mass in the above process is further secured by adding to it some sulphate of iron, calcined at a red heat with one-tenth its weight of nitre, so as to have excess of peroxide of iron present; in

that case no arseniate of cobalt is formed. Great care must also be taken entirely to expel the excess of sulphuric acid from the bisulphate of potassa, by adequate exposure to a red heat.

Cobalt is of a reddish-gray colour, brittle, and difficultly fusible. Its specific gravity, according to Bergman, is 7·7: according to Turner, 7·834. Tassaert and Lampadius place it at 8·5 and 8·7. The specific heat of a specimen of cobalt not quite pure, as determined by Regnault, was = 0·11712; that of pure cobalt, reduced from the oxalate, being = 0·10696. It is not magnetic when perfectly pure. Its equivalent is 30. (29·5 GMELIN and TURNER, 29·57 GRAHAM.)

COBALT AND OXYGEN unite in two proportions, forming oxides corresponding with those of iron, namely, a *protoxide* and a *sesquioxide*.

PROTOXIDE OF COBALT (*cob* + *o*) or *CoB*, is formed by adding potassa to the nitrate, and washing and drying the precipitate; it appears very dark blue or nearly black. By exposure to heat and air it absorbs an additional portion of oxygen, and is thus converted into black *peroxide*. The protoxide, when recently precipitated and moist, is *blue*; and, if left in contact of water, becomes a *red hydrate*; and afterwards of a dingy green by absorbing oxygen.

The protoxide may also be obtained by heating the carbonate of cobalt out of contact of air; it is then of a greenish-gray colour. It is recognised by the facility with which it imparts a blue tint to vitrifiable compounds and to white enamel. It dissolves with the extrication of heat in nitric and sulphuric acid; and is known to be free from peroxide, by dissolving in hydrochloric acid without the evolution of chlorine. When hydrogen is passed over it at a red heat, it is decomposed, and porous metallic cobalt remains, which is sometimes pyrophoric. It consists of

				Rothoff.	Berthier.
Cobalt	1	30	78·9	78·67	78·75
Oxygen	1	8	21·1	21·33	21·25
Protoxide of cobalt	1	38	100·0	100·00	100·00

PEROXIDE OF COBALT. SESQUIOXIDE OF COBALT. (*cob* + $\frac{1}{2}$ *o*).—When either the finely-divided metal, or the protoxide, are heated in the air, they absorb oxygen, and acquire a dark-brown colour, forming an oxide intermediate between the peroxide and protoxide, and probably of indefinite composition; but according to Hess (POGGEND., xxvi. 542), consisting of ($3\text{Co} + 4\text{O}$). When chlorine is passed through a mixture of the hydrated protoxide and water, or when a solution of chloride of cobalt is decomposed by chloride of lime, a black precipitate falls, which is the *hydrated peroxide*, and which may be deprived of water by very cautious drying at a high temperature; it is then black, and insoluble in dilute acids; it does not form salts; when acted on by hydrochloric acid it evolves chlorine, and yields chloride of cobalt. It sometimes occurs *native*, but is very rare. It consists of

				Rothoff.
Cobalt	1	30	71·4	71·08
Oxygen	$\frac{1}{2}$	12	28·6	28·92
Sesquioxide of cobalt	1	42	100·0	100·00

CHLORIDE OF COBALT. (*cob + c.*)—Cobalt burns when heated in chlorine, and forms *chloride of cobalt*. When cobalt or oxide of cobalt is dissolved in hydrochloric acid, evaporated to dryness, and the residuum heated to redness out of the contact of air, a substance of a blue colour and micaceous texture is obtained, which is a pure chloride of cobalt, consisting of

				Brande.
Cobalt	1 . .	30 . .	45.4 . .	47.75
Chlorine	1 . .	36 . .	54.6 . .	52.25
<hr/>				
Chloride of cobalt	1	66	100.0	100.00

When the blue anhydrous chloride of cobalt is dissolved in water it yields a pink solution, which, if duly diluted, and written with, becomes invisible when dry; but if gently heated, the writing appears in brilliant blue, which soon vanishes as the paper cools, in consequence of the salt absorbing ærial moisture: if overheated, the writing blackens, in consequence of the decomposition of the chloride and the paper. This solution has been termed *Hellot's sympathetic ink*. Dr. Thomson states that it was first made known by Waitz, in 1705; a second time by Teichmeyer, in 1731; and, lastly, by Hellot, in 1737. (*Mém. Paris.*) If it contain copper, nickel, or iron, the writing appears green; hence, in what are termed *magic landscapes*, the sky is tinted with solution of pure chloride of cobalt, and the trees and grass with that which is cupreous. By careful evaporation, the solution of this chloride forms red crystals, in the form of oblique rhombic prisms (BROOKE, *Ann. of Phil.*, 2nd series, vii. 365), composed of 1 proportional of the chloride and 5 of water.

Dumas observes that chloride of cobalt may be obtained by passing chlorine over the finely-powdered ore of cobalt (glance cobalt). The chlorides of arsenic, sulphur, and iron, are volatilized, and the chloride of cobalt remains, provided only a moderate heat has been used.

IODIDE OF COBALT remains unexamined. No precipitate is produced in solutions of cobalt either by hydriodic acid, or iodide of potassium; or by iodic acid, or iodate of potassa.

BROMIDE OF COBALT is formed when cobalt is heated in bromine vapour; it is a green compound, which yields with water a red solution; it becomes purple when concentrated, and reverts to green when dry; it is also formed by boiling cobalt and bromine with water.

Bromide of cobalt is very deliquescent; it is fusible at a high red-heat, and undergoes slight decomposition; ammonia decomposes it, and in excess redissolves the precipitate. It consists of

Cobalt	1	30	27.7
Bromine	1	78	72.3
Bromide of cobalt	1	108	100.0

FLUORIDE OF COBALT.—When oxide of cobalt is digested in hydro-fluoric acid, a pink solution is obtained, which yields crystals on evaporation, difficultly soluble in water.

NITRATE OF COBALT.—With nitric acid the oxide of cobalt furnishes a brownish-red deliquescent salt in irregular rhombic crystals, consisting,

according to Dr. Thomson, of 1 proportional of oxide of cobalt, 1 of nitric acid, and 6 of water. It is soluble in alcohol. It is easily resolved by heat into nitrous acid, oxygen, and peroxide of cobalt.

AMMONIATED OXIDE OF COBALT. COBALTE OF AMMONIA.—It is doubtful whether any binary compound of ammonia and oxide of cobalt exists. Salts of cobalt with excess of acid are not precipitated by ammonia, nor by ammoniacal salts, because double salts are formed. From a neutral solution of cobalt, ammonia throws down a portion of oxide in the form of blue hydrate, which remains unchanged, provided air be excluded; but, if air has access, oxygen is absorbed, and the precipitate first becomes green, and then dissolves into a brown fluid, which appears to be a compound of *cobaltate of ammonia* with the other ammoniacal salt. L. Gmelin supposes the *cobaltic acid* to consist of 1 equivalent of cobalt and 2 of oxygen; its ammoniacal solution is apt to deposit peroxide of cobalt, in which case it also gives out nitrogen.

AMMONIO-NITRATE OF COBALT.—When excess of ammonia is added to nitrate of cobalt, part of the oxide is thrown down, and the remainder forms a double salt, which crystallizes in rose-coloured cubes of a saline and urinous taste. At a red heat it fuses like nitrate of ammonia, and leaves peroxide of cobalt. The alkalis do not decompose it, but the sulphurets give a black precipitate. (THENARD.)

PROTOSULPHURET OF COBALT. (*cob + s*).—When 1 part of carbonate of soda, 2 of sulphur, and 1 of pulverized (native) arsenio-sulphuret of cobalt, are heated together, sulphuret of sodium, of arsenic, and of cobalt, are formed, and on cooling, the sulphuret of cobalt separates in bronze-coloured scales. When the fused mass is washed, if the ore was pure, sulphuret of cobalt is the only insoluble residue, the double sulphuret of arsenic and sodium being dissolved. Sulphuret of cobalt may also be obtained by heating sulphate of cobalt with charcoal, but in that case some metallic cobalt is blended with it, for carbon decomposes the sulphuret of cobalt. It is thrown down in the state of hydrate when protosalts of cobalt are decomposed by sulphuretted hydrogen.

Protosulphuret of cobalt is yellow, resembling magnetic pyrites in colour; it fuses at a red heat, and is easily soluble in acids. (BERTHIER.) It consists of

Cobalt	1	30	65.3
Sulphur	1	16	34.7
Protosulphuret of cobalt	1	46	100.0

Oxysulphuret of cobalt is formed when hydrogen is passed over heated sulphate of cobalt.

SESQUISULPHURET OF COBALT (*cob + 1½s*) is obtained by decomposing sulphate of cobalt by sulphuretted hydrogen (ARFWEDSON, *Ann. of Phil.*, 2nd series, vii.), or by passing sulphuretted hydrogen over peroxide of cobalt. (SOTTERBERG.) A *native sesquisulphuret of cobalt* is found in Sweden and Prussia of a light steel-gray colour, not crystallized, and generally blended with pyrites; it contains cobalt and sulphur in the relative proportions of

Cobalt	1	30	58.5
Sulphur	$1\frac{1}{2}$	24	41.5
<hr/>			
Sesquisulphuret of cobalt	1	54	100.0

BISULPHURET OF COBALT ($\text{cob} + 2\text{S}$) was obtained by Sotterberg by heating peroxide of cobalt with 3 times its weight of sulphur, and treating the product with hydrochloric acid to decompose any protosulphuret, and afterwards with solution of potassa to abstract the excess of sulphur: the bisulphuret remains in the form of a black powder insoluble in hydrochloric acid; it consists of

Cobalt	1	30	48.4
ulphur	2	32	51.6
<hr/>			
Bisulphuret of cobalt	1	62	100.0

SULPHITE AND HYPOSULPHITE OF COBALT have not been examined.

HYPOSULPHATE OF COBALT forms, according to Heeren, a red saline mass, very soluble, but not deliquescent: he obtained it by the decomposition of sulphate of cobalt by hyposulphate of baryta. The crystals, which are difficultly obtained, contain

Oxide of cobalt	1	38	23.2
Hyposulphuric acid	1	72	43.9
Water	6	54	32.9
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Crystallized hyposulphate of cobalt	1	164	100.0

SULPHATE OF COBALT ($\text{COB} + \text{S}'$) forms oblique rhombic prisms, like sulphate of iron (BROOKE, *Ann. of Phil.*, vi. 120, 2nd series), of a bitterish metallic taste, soluble in 24 parts of water at 60° , and insoluble in alcohol. It may be made by dissolving the newly-precipitated protoxide or carbonate of cobalt in sulphuric acid diluted with its bulk of water, but is not easily crystallized. When dried at a temperature of 500° , the crystals fall into a blue powder, which, in a red heat, fuses, but does not give off acid except at a very high temperature. The blue powder is the *anhydrous sulphate of cobalt*, perfectly soluble in water, and forming a pink solution; it is slightly deliquescent, and becomes lilac-coloured by exposure to air. It consists of

Oxide of cobalt	1	38	48.7	Rothoff. 47.89	Brande. 50
Sulphuric acid	1	40	51.3	52.11	50
<hr/>					
Anhydrous sulphate of cobalt	1	78	100.0	100.00	100

The crystals consist of

Anhydrous sulphate of cobalt	1	78	59.1	Bucholz. 56	Mitscherlich. 57.3	Proust. 58
Water	6	54	40.9	44	42.7	42
<hr/>						
Crystals of sulphate of cobalt	1	132	100.0	100	100.0	100

When 1 part of sulphate of cobalt and 2 or 3 of sulphate of zinc are dissolved together and precipitated by carbonate of soda, a precipitate falls, which has been called a cobaltate of zinc; when washed and calcined it acquires a green colour, and has been used as a pigment, under the name of *Rinmann's green*.

BISULPHATE OF COBALT is formed by digesting the sulphate in excess of acid; the solution affords long four-sided prismatic efflorescent crystals, composed of 1 proportional of protoxide of cobalt, 2 of sulphuric acid, and 3 of water. (THOMSON.)

AMMONIO-SULPHATE OF COBALT.—Sulphate of cobalt forms a double salt with ammonia. If it contain nickel, the crystals are of a greenish tinge, but pink when the cobalt is pure. When anhydrous sulphate of cobalt is exposed to ammonia it increases in bulk, heats, and falls into a white powder with a slight tint of red. 100 parts of the salt take up 66.48 of ammonia. (H. ROSE, *Ann. de Ch. et Ph.*, LXII. 313.)

SULPHATE OF COBALT AND POTASSA.—A double salt, isomorphous with the ammonio-magnesian sulphate, and less soluble, and more easily crystallized than the sulphate of cobalt. The crystals include 1 atom of sulphate of cobalt, 1 of sulphate of potassa, and 6 of water. (MITSCHERLICH.)

SELENIURET OF COBALT has a gray metallic lustre and foliated fracture.

SELENITE OF COBALT is an insoluble rose-coloured powder.

PHOSPHURET OF COBALT is a white brittle compound, obtained by projecting phosphorus upon red-hot cobalt, or by calcining a mixture of superphosphate of lime, oxide of cobalt, and charcoal; it burns before the blowpipe and tarnishes by exposure to air. It contains about 20 per cent. of phosphorus (PELLETIER); it consists, therefore, probably of

Cobalt	2	60	79
Phosphorus	1	16	21
Phosphuret of cobalt	1	76	100

Rose obtained a *subsesquiphosphuret of cobalt* by exposing subphosphate of cobalt to the action of hydrogen; he represents it as consisting of 3 atoms of cobalt and 2 of phosphorus.

HYPOPHOSPHITE OF COBALT forms, according to Rose, octoëdral efflorescent crystals containing 49.35 per cent. of water of crystallization.

Nothing is known respecting the *Phosphite of Cobalt*.

PHOSPHATE OF COBALT may be formed by double decomposition, as by adding phosphate of soda to chloride of cobalt; it is insoluble in water, of a lilac colour, and soluble in excess of phosphoric acid; if mixed with pure alumina, and exposed to heat, it produces a beautiful blue colour, which may sometimes be employed by painters as a substitute for ultramarine: a pure salt of cobalt free from nickel, and pure alumina free from iron, are essential to the production of a fine blue. The alumina and the phosphate are most conveniently mixed when both are recently precipitated and in the hydrated state; 8 parts by bulk of alumina are thus well-mixed with 1 part of the phosphate, and then dried and heated to redness; the crucible is allowed to remain in the fire till the charcoal is consumed. This compound, from its discoverer, is called *Thenard's blue*.

CARBONATE OF COBALT (COB + CAR) is formed by decomposing the nitrate, chloride, or sulphate of cobalt, by carbonate of potassa or soda: a purple powder is precipitated, becoming pink when dried, and readily

soluble with effervescence in the acids. Heated in close vessels it gives off carbonic acid, and a gray protoxide of cobalt remains. It dissolves in excess of carbonic acid, and in alkaline carbonates. According to Dumas, the precipitate thrown down from sulphate of cobalt by carbonate of potassa is a sesquicarbonate of cobalt: it is of a rose-colour; excess of carbonate of potassa dissolves much of this precipitate, because carbonic acid is set free and produces bicarbonate, in which the carbonate of cobalt is soluble; the solution has a violet tint; by boiling, the whole of the carbonate is thrown down. The carbonate of cobalt which is formed by precipitation with the alkaline bicarbonates, retains its colour when dry.

AMMONIO-CARBONATE OF COBALT.—Carbonate of cobalt is readily soluble in solution of carbonate of ammonia, forming a bright pink liquid.

CYANURET OF COBALT.—Hydrocyanic acid, added to acetate of cobalt, throws down the whole of the metal in the form of cyanuret.

FERROCYNANURET OF COBALT.—Ferrocyanuret of potassium gives a greenish yellow or gray precipitate, and ferrosesquicyanuret a brown precipitate, in solutions of cobalt: these precipitates are insoluble in hydrochloric acid.

COBALTOCYANURET OF POTASSIUM.—Cyanuret of cobalt is dissolved in a solution of cyanuret of potassium; or hydrocyanic acid is added to a solution of cyanuret of cobalt, or of carbonate of cobalt, in potassa, till it no longer reddens turmeric; on evaporation, transparent shining prismatic crystals are obtained, which are neutral to vegetable colours, decrepitate when heated, and then fuse into a dark olive-green liquid. This salt is easily soluble in water, and the solution is nearly colourless. The pink precipitate which it produces in the salts of cobalt, is, perhaps, analogous to Prussian blue. (L. GMELIN.) This salt is anhydrous, and consists of

	L. Gmelin.			
Potassium . . .	3	120	35.7	35.23
Cobalt . . .	2	60	17.9	17.19
Cyanogen . . .	6	156	46.4	47.58
	1	336	100.0	100.00

SULPHOCYANURET OF COBALT.—Sulphate of cobalt is added to an alcoholic solution of sulphocyanuret of potassium; sulphate of potassa falls, and the blue solution yields prismatic crystals which deliquesce in the air into a liquid, at first violet-coloured, then red, and yielding a nearly colourless solution in water, which, on the addition of alcohol, again becomes blue. (GROTHUSS, *Gilbert's Ann.*, Lxi. 70.)

BORATE OF COBALT.—Solution of borax occasions a pink precipitate in solution of chloride of cobalt, which is a *borate of cobalt*, and which produces a beautiful blue glass when fused.

USES OF COBALT.—The *alloys of cobalt* are unimportant. The chief use of cobalt is in the state of *oxide* as a colouring material for porcelain, earthenware, and glass; it is principally imported from Germany in the state of *zaffre*, and *smalt* or *azure*. *Zaffre* is prepared by calcining the ores of cobalt, by which sulphur and arsenic are volatilized, and an impure oxide of cobalt remains, which is mixed with about twice its weight of

finely-powdered flints. *Smalt* and *azure blue* are made by fusing zaffre with glass; or by calcining a mixture of equal parts of roasted cobalt ore, common potash, and ground flints. In this way a blue glass is formed, which, while hot, is dropped into water, and afterwards reduced to a very fine powder. Thenard's blue is also a valuable pigment.

CHARACTERS OF THE SALTS OF COBALT.—Solution of potassa produces a blue precipitate in solutions of cobalt, which becomes green, and if boiled, or long kept, dirty red. It is not redissolved by excess of potassa. Ammonia forms a blue precipitate in solutions of cobalt, which, on its further addition, becomes green, and mostly dissolves: this solution becomes brown by exposure to air. Carbonate of ammonia produces a red precipitate, which dissolves in hydrochlorate of ammonia. Hydro-sulphuret of ammonia produces a black precipitate, even when the cobaltic solution is excessively dilute. Those salts of cobalt which are insoluble in water, are nearly all soluble in dilute sulphuric or hydrochloric acid, and are generally thrown down by ammonia, and blackened by hydrosulphuret of ammonia. When no precipitate is produced in an acidulated metallic solution by sulphuretted hydrogen gas, while at the same time a black precipitate is produced in the neutral or alkaline solution, by hydrosulphuret of ammonia, scarcely any other metal than cobalt, nickel, or iron, can be present. (H. ROSE.) Before the blowpipe, cobalt and its compounds colour borax and microcosmic salt blue. By charcoal they are reduced to a gray powder which is metallic cobalt. (BERZELIUS.) Cobalt is not thrown down in the metallic state by any of the other metals.

§ XIV. NICKEL.

NICKEL was discovered by Cronstedt, in 1751. Its commonest ore was termed by the German miners, *kupfernickel*, or “false copper:” it is an arsenuret of nickel; it occurs most abundantly in the mines of Saxony and Germany; it has also been found in Dauphiny, Cornwall, and several other localities: there is also a native sulphuret of nickel; what is frequently termed *native nickel* is a variety of the arsenuret.

The common commercial source of nickel is an artificial arsenuret, known under the name of *Speiss*; it generally contains between 50 and 60 per cent. of nickel, and, as has been observed by Wöhler, it occasionally forms octoëdral crystals, consisting of 1 atom of arsenic and 1.5 of nickel.

An abstract of the numerous processes which have been proposed for obtaining pure nickel will be found in Dumas (*Chim. app. aux Arts*, iii, 253). It is easily procured *nearly* pure; the difficulty consists in *perfectly* freeing it from all traces of other substances, and especially of cobalt. One of the simplest modes of proceeding is as follows:—Dissolve the impure arsenuret, sold under the name of *speiss*, finely-pulverized, in sulphuric acid diluted with 3 parts of water, by adding the quantity of nitric acid necessary to produce the solution. When cool filter this solution, concentrate it, and set it aside: crystals of sulphate of nickel make their appearance. Proceed in this manner till a sufficient quantity of crystals has been obtained; dissolve and crystallize a second and third time. Then redissolve the purified crystals, and pass sulphuretted

hydrogen through the solution, which should be slightly acidulated, to precipitate any copper or arsenic that may be present; boil, filter, and recrystallize. The crystals now obtained furnish a solution from which oxide of nickel is thrown down by potassa: it may, however, still retain cobalt, which is separated by diffusing the hydrated precipitate through water, and subjecting it to a current of chlorine, by which the cobalt is thrown down (with some nickel) in the form of peroxide, and a solution of chloride of nickel is obtained, from which the pure hydrated oxide of nickel may now be thrown down, by potassa; or, if intended for the production of the metal, by oxalic acid in the state of *oxalate*; which is then dried, and intensely heated in a covered crucible: it affords a button of pure nickel; the metal may also be obtained by exposing a mixture of lamp-black and oxide of nickel, made into a paste with oil, to a heat gradually raised to whiteness. The above process is improved by thoroughly roasting the powdered speiss previous to its solution, and by adding to the solution of the first crop of crystals of sulphate of nickel a sufficient quantity of sulphate of potassa, so as to yield, on evaporation, the double sulphate of nickel and potassa: this double salt is then to be treated by sulphuretted hydrogen as above directed.

Nickel is a white brilliant metal, which acts upon the magnetic needle, and is itself capable of becoming a magnet. Its magnetism is more feeble than that of iron, and vanishes at a heat somewhat below redness (630° FARADAY). It is ductile and malleable: I have a Bavarian coin struck in nickel; the impression of the die is very perfect. Its specific gravity varies from 8.27 to 8.40 when fused, and after hammering, from 8.69 to 9.00. Its specific heat is 0.10863. It is not oxidized by exposure to air at common temperatures, but when heated in the air it acquires various tints like steel; at a red heat it becomes coated by a gray oxide: before the oxygen blowpipe it burns with sparks, somewhat like iron: its equivalent number, deduced from various analyses of its compounds, is between 26 and 30. I have assumed it at 28. (29.5 GMELIN and TURNER, 26 THOMSON.)

PROTOXIDE OF NICKEL, ($\text{NiO} + \text{O}$), or NiO , is obtained by adding potassa to the solution of the pure nitrate or sulphate; a precipitate falls of a pale-green colour, which is a *hydrated protoxide*; this, heated to redness, affords a gray protoxide. The carbonate, oxalate, or nitrate of nickel, heated to redness, also afford the protoxide in the form of a gray powder: when intensely heated out of contact of air it becomes green. It is not magnetic. This oxide, in the state of hydrate, easily dissolves in ammonia, forming a sapphire-blue solution; this property is often made use of to separate oxides of nickel and iron, the latter (peroxide) being insoluble in ammonia. Protoxide of nickel consists of

				Klaproth.	Richter.	Thomson.	Rothoff.
Nickel	1	28	77.78	77	77.82	78	78.55
Oxygen	1	8	22.22	23	22.18	22	21.45
Protoxide of nickel	1	36	100.00	100	100.00	100	100.00

The hydrated oxide when collected upon a filter is apple-green, and retains its colour when washed and dried, becoming pulverulent: it may

be obtained in crystals by boiling carbonate of nickel in ammonia; carbonate of ammonia and hydrated oxide of nickel are formed. (TUPPUTI.) It consists of

Protoxide of nickel	1	36	80	Proust.
Water	1	9	20	79
<hr/>				21
Hydrated protoxide of nickel	1	45	100	100

PEROXIDE OF NICKEL. SESQUIOXIDE OF NICKEL. (*nic* + $1\frac{1}{2}$ O.)—If excess of chlorine be passed through a mixture of the hydrated oxide and water, a black powder is gradually formed, which, when acted upon by sulphuric acid, evolves oxygen, and returns to the state of protoxide: with hydrochloric acid it yields chlorine. Ammonia dissolves it with the evolution of nitrogen, and forms a solution of the protoxide. It is not a salifiable base. It consists of

Nickel	1	28	70	Rothoff.	Lassaigne.
Oxygen	$1\frac{1}{2}$	12	30	70·95	71·43
<hr/>				29·05	28·57
Sesquioxide of nickel	1	40	100	100·00	100·00

CHLORIDE OF NICKEL. (*nic* + *c.*)—When finely-divided nickel is heated in chlorine, the gas is absorbed, the metal burns, and a golden-coloured *chloride* results. This compound may also be obtained by dissolving nickel or its oxide in hydrochloric acid, evaporating to dryness, and heating the residue to redness in a glass tube; it then remains in the form of a yellow lamellar substance, volatile at a high red-heat, which dissolves in hot water, and leaves on evaporation a confusedly crystalline mass, of an apple-green colour and sweetish taste. Chloride of nickel consists of

Nickel	1	28	43·7
Chlorine	1	36	56·3
<hr/>			
Chloride of nickel	1	64	100·0

AMMONIO-CHLORIDE OF NICKEL.—100 parts of anhydrous chloride of nickel absorb 74·8 of ammonia, becoming a bulky white powder which yields a blue solution with water. (H. ROSE, *Ann. de Ch. et Ph.*, Lxii. 317.) When hydrochlorate of ammonia and chloride of nickel are dissolved together in atomic proportions, a very soluble and difficultly-crystallizable double salt is obtained on evaporation. (TUPPUTI.)

IODIDE OF NICKEL may be formed by adding solution of iodide of potassium to sulphate or nitrate of nickel; it falls in the form of a greenish-yellow precipitate. According to Lassaigne, when nickel and iodine are heated together in a glass tube, a brown fusible mass is formed, containing about 24 per cent. of nickel.

BROMIDE OF NICKEL.—The vapour of bromine is absorbed by filings of nickel, forming a brown compound; when heated it assumes the appearance of *aurum musivum*, and at a very high temperature it partly sublimes in yellow micaceous scales, and begins to decompose. This bromide is also formed when nickel and bromine are boiled in water; the solution is green, becomes brown by evaporation, and yields small whitish acicular crystals, very deliquescent. The solution of bromide of

nickel exposed to the air, deposits flocks of oxide of nickel: evaporated to dryness a reddish deliquescent bromide remains, soluble in alcohol, ether, hydrochloric acid, and ammonia. At a high red-heat in contact of air it is decomposed, bromine is evolved, and oxide of nickel remains. (DUMAS.)

FLUORIDE OF NICKEL, obtained by dissolving the hydrated oxide in hydrofluoric acid, yields green irregular crystals, and forms double salts with ammonia and with potassium.

NITRATE OF NICKEL.—Nitric acid acts upon nickel with disengagement of nitric oxide, and a bright green solution of protoxide is obtained, which by careful evaporation yields prismatic crystals of protonitrate of nickel: exposed to heat, part of the acid may be driven off so as to leave a green insoluble subnitrate, and this at a higher temperature is decomposed, peroxide, or ultimately protoxide, of nickel remaining. The crystals of nitrate of nickel effloresce in dry air, but deliquesce in a damp atmosphere; they are soluble in 2 parts of water at 60°, and also in alcohol: they consist, according to Thomson, of

Protoxide of nickel	1	36	26.7
Nitric acid	1	54	40.0
Water	5	45	33.3
Crystallized nitrate of nickel	1	135	100.0

AMMONIA AND OXIDE OF NICKEL.—When hydrated oxide of nickel is digested in ammonia it readily dissolves and forms a deep-blue solution, the shade of which is paler when the oxide predominates. When heated, it deposits granular crystals of hydrated oxide: exposed to air, it gradually deposits *ammonio-carbonate of nickel*. The fixed alkalis throw down oxide of nickel, combined with the alkali used.

AMMONIO-NITRATE OF NICKEL.—When ammonia is added in excess to nitrate of nickel and the solution evaporated, green crystals of this double salt are obtained: the alkalis do not render their solution turbid, but the hydrosulphurets throw down the nickel. (THENARD, *Ann. de Ch.*, xliii. 245.)

SULPHURET OF NICKEL (*nic + s*) may be formed by fusion, or by heating oxide of nickel with sulphur, or by passing sulphuretted hydrogen over the heated protoxide. It is yellow, and resembles pyrites. When sulphuretted hydrogen is passed into a perfectly neutral solution of nickel, a part of the metal falls in the form of a black hydrated sulphuret; if the solution be acid, the metal is not thus precipitated: hence the method of separating nickel from certain other metals, such as copper and arsenic, the precipitation of which is not prevented by excess of acid. When acetate of nickel is decomposed by sulphuretted hydrogen, the sulphuret of nickel has a peculiar brilliant metallic lustre. The hydrated sulphuret may be dried at 212° without losing its combined water. A sulphuret of nickel is also thrown down, when the soluble salts of nickel are decomposed by sulphuret of potassium. There is also a *native sulphuret of nickel*, which occurs in capillary filaments, of a yellow-gray colour. It is the *hair-pyrites* of the Germans. Sulphuret of nickel consists of

				Arfwedson.	E. Davy.	Rose. Native.
Nickel	1	28	63.6	64.35	66	64.8
Sulphur	1	16	36.4	34.26	34	35.2
Sulphuret of nickel	1	44	100.0	98.61	100	100.0

A *subsulphuret of nickel* is formed, according to Arfwedson, when hydrogen is passed over sulphate of nickel at a red heat, sulphurous acid and water being evolved: it is fusible and magnetic. Berthier obtained the same sulphuret by heating sulphate of nickel in a crucible lined with charcoal.

Neither the *Hyposulphite*, the *Sulphite*, nor the *Hyposulphate* of nickel have been examined.

SULPHATE OF NICKEL ($\text{NiC} + \text{S}'$) is formed by dissolving the oxide or carbonate of nickel in diluted sulphuric acid: concentrated sulphuric acid acts with difficulty on nickel even at a boiling heat. This salt yields emerald-green prismatic crystals, the form of which varies, depending, according to Phillips and Cooper (*Ann. of Phil.*, xxii. 489), upon variations in the water of crystallization; it is soluble in about 3 parts of water at 60° , and efflorescent by exposure; its taste is sweet and astringent; it is insoluble in alcohol and in ether. Exposed to heat, the crystals crumble down into a yellow powder; at a white heat the acid is expelled, and protoxide remains. It has been observed by Mitscherlich, that when the ordinary crystals (containing 7 atoms of water) are exposed in a close glass vessel to the sunshine, or when they are long kept, they become a congeries of small octoëdral crystals, which are opaque, but retain the original quantity of combined water. This salt is sometimes obtained by heating common nickel in sulphuric acid, with the occasional addition of nitric acid; though it is seldom pure when thus prepared. The anhydrous salt consists of

				Berthier.	Tupputi.
Oxide of nickel	1	36	47.4	47.8	46.6
Sulphuric acid	1	40	52.6	52.2	53.4
Anhydrous sulphate of nickel	1	76	100.0	100.0	100.0

The crystallized sulphate consists of

				Tupputi.	Mitscherlich.	R. Phillips.
						<i>sq. prism. rhombic p.</i>
Oxide of nickel	1	36	25.9	25.63	54.4	26.2
Sulphuric acid	1	40	28.8	29.37		30.0
Water	7	63	45.3	45.00	45.6	43.8
Crystals of sulphate of nickel	1	139	100.0	100.00	100.0	100.0

SULPHATE OF AMMONIA AND NICKEL is formed by evaporating a mixed solution of sulphate of ammonia and sulphate of nickel; it forms four-sided prismatic crystals, of a green colour, soluble in 4 parts of cold water, and consisting, according to Mitscherlich, of 1 atom of sulphate of ammonia, 1 of sulphate of nickel, and 8 of water. 100 parts of anhydrous sulphate of nickel absorb 65.91 of ammonia, evolving much heat, and forming a bulky white compound, with a tinge of violet. (H. ROSE, *Ann. de Ch. et Ph.*, lxii. 312.)

SULPHATE OF POTASSA AND NICKEL is obtained by adding potassa to sulphate of nickel (not in excess), filtering and evaporating; or by mixing

and evaporating the solution of sulphate of nickel, and sulphate of potassa. It forms pale green rhomboidal crystals, (BROOKE, *Ann. of Phil.*, vi. 438,) of a sweetish and bitter taste, soluble in 9 parts of cold water. (TUPPUTI, *Ann. de Chim.*, LXXVIII. and LXXIX.) It has been analyzed by Mitscherlich, and by Cooper (*Ann. of Phil.*, vi. 440), and consists of

				Mitscherlich.	Cooper.
Potassa	1	48	22.0	21.58	20.48
Oxide of nickel	1	36	16.5	17.10	17.54
Sulphuric acid	2	80	36.7	36.63	37.90
Water	6	54	24.8	24.69	24.08
Sulphate of potassa and nickel	1	218	100.0	100.00	100.00

SULPHATE OF NICKEL AND IRON is formed by mixing the solution of the two sulphates, or by dissolving the mixed protoxides in sulphuric acid, and evaporating the solution. It is a green efflorescent salt, in tabular crystals.

SULPHATE OF NICKEL AND ZINC is formed by mixing atomic proportions of the two sulphates in solution and evaporating: it forms prismatic crystals of a pale green colour, soluble in 3 parts of water at 60°, and efflorescent. (TUPPUTI.)

SELENIURET OF NICKEL has not been examined. *Selenite of Nickel* is a white insoluble powder whilst moist, but becomes pale green when dried. The *biselenite* is soluble, and yields a green gum-like residue on evaporation.

PHOSPHURET OF NICKEL is a brittle whitish compound, decomposed by exposure to heat and air. It is formed by the action of phosphorus upon red-hot nickel, and is more fusible than the pure metal. It contains, according to Pelletier, 83 nickel + 17 phosphorus; according to Lampadius, 87 nickel + 13 phosphorus.

HYPOPHOSPHITE AND PHOSPHITE OF NICKEL remain unexamined.

PHOSPHATE OF NICKEL, being nearly insoluble, is precipitated upon adding phosphate of soda to a solution of nickel. It is of a pale-green colour. Digested in phosphate of ammonia, a triple ammonio-phosphate of nickel is formed: it is insoluble in water.

CARBURET OF NICKEL occasionally remains in the form of a shining powder, when a button of the metal, which has long been fused in the contact of carbon, is dissolved in nitric acid. (ROSS and IRVING, *Ann. of Phil.*, ii.)

CARBONATE OF NICKEL is precipitated in the form of a green powder, when carbonate of soda is added to sulphate of nickel. When long washed with boiling-water it becomes nearly black. Dried in the air at the temperature of 60°, it retains its green colour. It dissolves in excess of carbonic acid. It has been analyzed by Thomson and by Berthier, its components when dried at 60° being

Oxide of nickel	1	36	43.9
Carbonic acid	1	22	26.8
Water	3	27	29.3
Carbonate of nickel	1	85	100.0

According to Berthier a hydrated sesquicarbonate of nickel, ($nic + o$) $+ 11(car + 2o) + 5q$, is formed when a salt of nickel is decomposed by bicarbonate of soda: it is a very light greenish powder, not altered by desiccation.

AMMONIO-CARBONATE OF NICKEL is a very soluble and difficultly-crystallizable salt. If its solution be heated, carbonic acid and ammonia are evolved, and hydrated oxide of nickel is thrown down.

BORATE OF NICKEL is a pale-green insoluble compound, easily formed by double decomposition: it is soluble in the stronger acids.

CYANURET OF NICKEL is thrown down when a soluble cyanuret is added to a solution of nickel, or when hydrocyanic acid is mixed with acetate of nickel. A *potasso-cyanuret of nickel* is formed when moist cyanuret of nickel is dissolved in cyanuret of potassium: it yields on evaporation yellow rhombic prisms. Similar double cyanurets may be formed with other bases: they were discovered by Wöhler.

FERROCYANURET OF NICKEL is precipitated in the form of a gray or greenish powder when solution of ferrocyanuret of potassium is added to the soluble salts of nickel.

ALLOYS OF NICKEL.—Of these alloys, there is one which requires particular notice, namely, that with *iron*, which forms a principal metallic ingredient in most *aërolites*, or *meteoric stones*. Though we really know nothing of the source or origin of these bodies, it has been ascertained upon satisfactory evidence, that they are not of terrestrial formation; and, consequently, their visits to the surface of our planet have awakened much speculation, and some experimental research.

In the first place, it deserves to be remarked, that we have evidence of the falling of stony bodies from the atmosphere in various countries, and at very remote periods. Such events have been recorded by the most accredited of the early historians. The first tolerably accurate narration of the fall of a meteoric stone relates to that of Ensisheim, near Basle, upon the Rhine. The account, which is deposited in the church, runs thus: "A.D. 1492, Wednesday, November 7, there was a loud clap of thunder, and a child saw a stone fall from heaven: it struck into a field of wheat, and did no harm, but made a hole there. The noise it made was heard at Lucerne, Villing, and other places: on the Monday, King Maximilian ordered the stone to be brought to the castle, and after having conversed about it with the noblemen, said the people of Ensisheim should hang it up in their church, and his Royal Excellency strictly forbade anybody to take anything from it. His Excellency, however, took two pieces himself, and sent another to Duke Sigismund of Austria. This stone weighed 255 lbs."

In 1627, 27th November, the celebrated Gassendi saw a burning stone fall on Mount Vaisir, in Provence: he found it to weigh 59 lbs. In 1672, a stone fell near Verona, weighing 300 lbs. And Lucas, when at Larissa, in 1706, describes the falling of a stone, with a loud hissing noise, and smelling of sulphur. In September, 1753, De Lalande witnessed this extraordinary phenomenon near Pont de Vesle. In 1768, no

less than three stones fell in different parts of France. In 1790, there was a shower of stones near Agen, witnessed by M. Darcet, and several other respectable persons. And on the 13th of December, 1795, a stone fell near Major Topham's house, in Yorkshire; it was seen by a ploughman and two other persons, who immediately dug it out of the hole it had buried itself in: it weighed 56 lbs. We have various other and equally satisfactory accounts of the same kind. All concur in describing a luminous meteor, moving through the air in a more or less oblique direction, attended by a hissing noise, and the fall of stony or semi-metallic masses, in a heated state. We have, however, evidence of another kind, amply proving the peculiar origin of these bodies. It is, that although they have fallen in very different countries, and at distant periods, when submitted to chemical analysis, they all agree in component parts; the metallic particles being composed chiefly of iron and nickel: the earthy of silica and magnesia.

Large masses of *native iron* have been found in different parts of the world, of the history and origin of which nothing very accurate is known. Such are the great block of iron formerly at Elbogen, in Bohemia; the large mass discovered by Pallas, weighing 1600 lbs., near Krasnojarsk, in Siberia; that found by Goldberry, in the great desert of Zara, in Africa; probably, also, that mentioned by Mr. Barrow, on the banks of the Great Fish-river in Southern Africa; and those noticed by Celis, Humboldt, and others in America, of enormous magnitude, some exceeding 30 tons in weight. That these should be of the same source as the other meteoric stones, seems at first to startle belief; but when they are submitted to analysis, and the iron they contain found alloyed with nickel, it no longer seems credulous to regard them as of meteoric origin. We find nothing of the kind in the earth. Two blocks of such iron were, in fact, observed to fall from a meteor, at Hradschina, near Agram, in Croatia, in 1751. In URE's *Chemical Dictionary* there is a full chronological list of meteoric stones. (ART. METEOROLITE.) See also *Annals of Philosophy*, N. S., vol. xii., p. 83.

To account for these uncommon visitations of metallic and lapideous bodies, a variety of hypotheses have been suggested.

Are they merely earthy matter, fused by lightning? Are they the offspring of any terrestrial volcano? These were once favourite notions; but we know of no instance in which similar bodies have in that way been produced, nor do the lavas of known volcanos in the least resemble these bodies; to say nothing of the inexplicable projectile force that would here be wanted. Those who have taken up this conjecture, have assumed one impossibility to account for what they conceive to be another, namely, that the stony bodies should come from any other source than our own globe.

The notion that these bodies come from the moon, is, when impartially considered, neither absurd nor impossible, for any power which would move a body 6000 feet in a second, that is, about three times the velocity of a cannon-ball, would throw it from the sphere of the moon's attraction into that of our earth. The cause of this projectile force may be a volcano, and if thus impelled, the body would reach us in about two days, and enter our atmosphere with a velocity of about 25,000 feet

in a second. Their ignition may be accounted for, either by supposing the heat generated by their motion in our atmosphere sufficient to ignite them, or by considering them combustible, and ignited by contact of air.

While we are stating the *possibility* of these opinions, it may be remembered, that, in the great laboratory of the atmosphere, chemical changes *may* happen, attended by the *production* of metals, though this is highly improbable: the disruption of small planetary bodies is a more plausible hypothesis.

Meteoritic stones have generally an uneven black surface, and are internally of a gray colour and coarse texture. When carefully examined, most of them appear made up of a number of small spherical bodies and metallic grains imbedded in a softer matter, composed, according to Mr. Howard (*Phil. Trans.*, 1802), of silica, magnesia, and iron with a little nickel; the spherical bodies are nearly of similar composition; and the metallic grains are partly *meteoric iron*, and partly the same with a little sulphur. In addition to these substances, Vauquelin found 2 per cent. of chrome in a stone which fell at Langres, in 1815. (*Ann. de Ch. et Ph.*, i. 53.) And Stromeyer detected cobalt in the meteoric iron from the Cape of Good Hope. (*THOMSON'S Annals*, ix.) Lime and alumina have also been found in them, and a small proportion of manganese. M. Laugier has announced the existence of a meteoric stone without nickel, but containing chrome; and as he has detected the latter metal in all the *aërolites* which he has examined, he considers it as their most characteristic ingredient. (*Mém. du Muséum*, vi., p. 233.)

In meteoric iron the proportion of nickel varies considerably. In a specimen from the Arctic region I found 3·2 per cent. (*Quart. Jour.*, vi. 369.) In that from Siberia, Mr. Children found nearly 10 per cent. The analysis may be performed by solution in nitro-hydrochloric acid; the iron is thrown down by excess of ammonia in the state of peroxide; it is separated by filtration, washed and dried; and on evaporating the filtrated liquor, and heating its dry residue red-hot, the oxide of nickel is obtained, which should be redissolved in nitric acid, and precipitated by pure potassa, the mixture being boiled for a few seconds. (*CHILDREN, Quart Jour.*, ix. 324.) The following are some further analyses of native iron. (*THOMSON'S Mineralogy*, i. 432.)

	Klaproth.		M. de Rivero and Boussingault.			
	Sclavonia.	Siberia.	From the Andes.			
Iron . . .	96·5	98·5	91·51	91·23	91·76	90·76
Nickel . . .	3·5	1·5	8·59	8·21	6·36	7·87
	100·0	100·0	100·10	99·44	98·12	98·63

Meteoric iron has been imitated by fusing iron with nickel. The alloy of 90 iron with 10 nickel is of a whitish-yellow cast, and not so malleable as pure iron. The alloy with 3 per cent. of nickel is perfectly malleable, and whiter than iron. These alloys are less disposed to rust than pure iron, but nickel alloyed with steel increases the tendency to rust. (*STODART and FARADAY, Quart. Jour. of Science and Arts*, ix.)

Nothing is known of the alloys of nickel with *potassium*, *sodium*, *manganese*, *zinc*, or *tin*. With *copper*, it forms a hard white alloy; the *white copper* of the Chinese, or *Pakfong* (p. 826), which consists, according

to the analysis of Dr. Fyfe, of 40·4 parts of copper, 31·6 of nickel, 25·4 of zinc, and 2·6 of iron. A similar alloy is often used as a substitute for silver, or for plated articles, under the name of *German silver*: it should consist of 1 part of nickel, 1 of zinc, and 2 of copper; or, when intended for *rolling*, of 25 parts of nickel, 20 of zinc, and 60 of copper; to which, if for *casting*, 3 of lead may be added. (GERSDORF, *Quarterly Journal*, i., 1827, 483.) The following details respecting the alloys of nickel are from a pamphlet on the subject by Messrs. Topping. (London, 1836.) The metals referred to should be as pure as possible. (1.) *Common German Silver*.—Copper 8, Nickel 2, Zinc $3\frac{1}{2}$. This is the commonest that can be made, with any regard to the quality of the article produced. It might do for wire, for common purposes. If the quantity of the nickel be reduced much below this, the alloy will be little better than pale brass, and tarnish rapidly. (2.) *Good German Silver*.—Copper 8, Nickel 3, Zinc $3\frac{1}{2}$. This is a very beautiful compound. It has the appearance of silver a little below standard; by some persons it is even preferred to the more expensive compounds. We strongly recommend manufacturers not to use a metal inferior to this. (3.) *Electrum*.—Copper 8, Nickel 4, Zinc $3\frac{1}{2}$. This is the compound we first introduced. We still prefer it to any of the others, and we think the public in general would do the same. It has a shade of blue, like very highly-polished silver: it tarnishes less easily than silver. (4.) Copper 8, Nickel 6, Zinc $3\frac{1}{2}$. This is the richest in nickel that can be made, without injuring the mechanical properties of the metal. It is a very beautiful compound, but requires a higher heat for fusion than the preceding, and will be found rather more difficult to work. (5.) *Tutenag*.—Copper 8, Nickel 3, Zinc $6\frac{1}{2}$. These proportions we originally obtained by analyzing a piece of Chinese tutenag, of the best ordinary quality; but have seen some rare specimens of Chinese tutenag equal to electrum, No. 3. This alloy is very fusible, but very hard, and not easily rolled: it is best adapted for casting. A variety of articles are now plated with nickel by electrolytic precipitation from a solution of sulphate of nickel, the process being in all respects similar to that in which copper is used (p. 308).

CHARACTERS OF THE SALTS OF NICKEL.—These salts have a rough metallic taste, and excite vomiting when swallowed in sufficient quantity. They are recognised by the peculiar green colour of their aqueous solutions, by the green precipitate which they afford with the fixed alkalis and their carbonates, and by giving a green precipitate with ammonia, soluble in excess of that alkali, when it assumes a blue colour. The yellow-green precipitate afforded by iodide of potassium, is very characteristic of nickel; but the nicest test of its presence is the ferrocyanuret of potassium, which produces a pale-gray or greenish-white precipitate in all the neutral solutions of the metal. To detect the presence of nickel in iron, Dr. Wollaston recommends that a small portion, which need not exceed ·01 of a grain, should be filed from the sample, and dissolved in a drop of nitric acid; evaporate this to dryness, and add a drop or two of liquid ammonia, which, when gently warmed, will dissolve any oxide of nickel that may be present. The transparent part of the fluid is then to be conducted by the end of a glass rod to a small distance from the precipitated oxide of iron, and mixed with a drop of the ferrocyanuret,

which, if nickel be present, will cause an immediate milkiness, not discernible when a solution of common iron is formed and treated in the same way. It must, however, be recollected in using this test, that the ferrocyanuret precipitate is taken up by excess of ammonia, giving a reddish solution, which, as the ammonia evaporates, forms a flocculent deposit of a silky appearance and of a buff tinge. Nickel is not precipitated in a metallic form by any metal except iron, which is slow and imperfect in its operation. Zinc, immersed in a solution of chloride of nickel, becomes covered with a suboxide, or a mixture of the metal and its protoxide. The acid solutions of nickel are not precipitated by sulphuretted hydrogen, nor by ammonia; the latter renders them blue. The alkaline sulphurets give black precipitates of hydrated sulphuret of nickel, which is slightly soluble in excess of those precipitates. Nickel has a great tendency to form double salts, which are only partially decomposed by the alkalis.

Before the blowpipe oxide of nickel becomes black at the extremity of the exterior flame, and in the interior greenish-gray. It is dissolved readily, and in large quantity, by microcosmic salt. The glass, while hot, is a dirty dark-red, which becomes paler and yellowish as it cools. After the glass has cooled, it requires a large addition of the oxide to produce a distinct change of colour. It is nearly the same in the exterior and interior flame, being slightly reddish in the latter. Nitre added to the bead makes it froth, and it becomes red-brown at first, and afterwards paler. It is easily fusible with borax, and the colour resembles the preceding. When this glass is long exposed to a high degree of heat in the interior flame, it passes from reddish to blackish and opaque, then blackish-gray and transparent; then paler reddish-gray and clearer; and lastly, transparent, and the metal is precipitated in small white metallic globules. The red colour seems here to be produced by the entire fusion or solution of the oxide, the black by incipient reduction, and the gray by the minute metallic particles before they combine and form small globules. When a little soda is added to the glass formed with borax, the reduction is more easily effected, and the metal collects itself into one single globule. When this oxide contains iron, the glass retains its own colour while hot, but assumes that of the iron as it cools.

§ XV. COPPER.

COPPER, *Cuprum*, or *Venus*, of the alchymists (♀), was known in the early ages of the world, and was the principal ingredient in domestic utensils, and in the instruments of war, previous to the discovery of malleable iron. The word *copper* is derived from the island of *Cyprus*, where it was first wrought by the Greeks. It is found *native*, and in various states of combination. Of its *ores*, the oxide, chloride, sulphuret, sulphate, phosphate, carbonate, and arseniate, are the most remarkable.

The metal may be obtained perfectly pure by dissolving the copper of commerce in nitric acid, with the addition of a little sulphuric acid; the solution is diluted, and a plate of iron is immersed, upon which the copper is precipitated; after having been previously washed in dilute sulphuric acid to separate a little iron that adheres to it, it may be fused into a button.

Copper, with the exception of titanium, is the only metal which has a red colour: it has much lustre, is very malleable and ductile, and exhales a peculiar smell when warmed or rubbed. It melts at a cherry-red or dull-white heat; or, according to Daniell, at a temperature intermediate between the fusing-points of silver and gold = 1996° Fahr. Its specific gravity varies from 8.86 to 8.89; the former being the least density of cast copper, the latter the greatest of rolled or hammered copper. Under a flame urged by oxygen gas, it takes fire, and burns with a beautiful green light. Exposed for a long time to damp air, copper becomes covered with a thin greenish crust of carbonate. If heated and plunged into water, a quantity of reddish scales separate, consisting of an imperfect oxide. The same scales fly off during cooling from a plate of the metal which has been heated red-hot. Copper does not decompose water at a red heat. The equivalent of copper is 32. (31.6 TURNER, 31.71 GRAHAM, 32 GMELIN.)

Native copper occurs in a variety of forms; massive, dendritic, granular, and crystallized in cubes, octoëdra, &c. It is found in Cornwall, Siberia, Saxony, Hanover, Sweden, and America; chiefly, but not exclusively, in primitive rocks.

COPPER AND OXYGEN. DIOXIDE OF COPPER. — There is only one salifiable oxide of copper, which, therefore, is generally regarded as the *protoxide*; but there is a *suboxide*, or *dioxide* ($2\text{Cu} + \text{O}$), which occurs *native*, and which may be formed artificially, not by the direct oxidization of copper, but by processes in which oxygen is abstracted from the protoxide. The following are the methods by which this suboxide may be obtained:—1. By heating 5 parts of peroxide with 4 of very finely divided metallic copper; or, according to Turner, by arranging thin copper plates one above the other, with interposed strata of the black oxide, and exposing them to a red heat carefully protected from the air. 2. By boiling a solution of acetate of copper with sugar, by which the protoxide of the acetate is reduced to the state of suboxide, and separates in the form of a red powder. 3. By fusing dichloride of copper with carbonate of soda, and washing and drying the residue. 4. By fusing a mixture of 100 parts of crystals of sulphate of copper, with 57 of crystals of carbonate of soda; when the water is expelled, the mass is reduced to powder, mixed with 25 parts of copper-filings, and exposed to a white heat for about 20 minutes; the residue is then pulverized, washed, and dried: it is of a red colour, the tint being improved by trituration and washing. This, which is Malaguti's process, is the most economical and yields the best product. (*Ann. de Ch. et Ph.*, liv. 216.) 5. *Hydrated* suboxide of copper is precipitated in the form of a dingy orange-coloured or brown powder, when a hot solution of subchloride of copper is decomposed by potassa: if dried in vacuo it becomes reddish-brown. 6. When sulphate of copper and protosulphate of iron are dissolved in water and precipitated by an alkali, dioxide of copper and peroxide of iron are thrown down: the former may be separated by digestion, out of the contact of air, in ammonia, which gives a colourless solution. (LEVOL, *Ann. de Ch. et Ph.*, lxx. 320.)

When this oxide is intensely heated out of contact of air, it frequently happens that small octoëdral and cubic crystals are formed in it; the

same thing was observed by Chenevix, on exposing peroxide or hydrate of copper to a violent heat, in an open crucible, without addition; a semi-fused mass, resembling native red copper, was obtained. (*Phil. Trans.*, 1801.) The dilute acids resolve this oxide into metallic copper and peroxide; it dissolves in concentrated hydrochloric acid; it also dissolves in ammonia, as will presently be explained; it is not soluble in solutions of potassa or of soda.

This compound may be regarded as consisting of 1 atom of copper and 1 of protoxide; or of

				Chenevix.	Berzelius.
Copper	2 . .	64 . .	88.9 . .	88.5 . .	88.97
Oxygen	1 . .	8 . .	11.1 . .	11.5 . .	11.03
Dioxide of copper	1	72	100.0	100.0	100.00

Copper vessels, such as tea-urns, &c., and medals, are often superficially coated with this oxide, or *bronzed*; it gives them an agreeable appearance, and prevents tarnish. For this purpose two processes are resorted to:—1. The copper surface is cleaned, and then brushed over with peroxide of iron (generally colcothar) made into a paste with water, or with a very dilute solution of acetate of copper; heat is then cautiously applied in a proper furnace or muffle, till it is found, on brushing off the oxide, that the surface beneath has acquired its proper hue. 2. 2 parts of verdigris and 1 of sal-ammoniac are dissolved in vinegar: the solution is boiled in a pipkin, skimmed, and diluted with water till it only tastes slightly of copper and ceases to deposit a white precipitate; it is then poured into another pipkin or copper-pan, and rapidly brought to boil, and the medal, previously rendered bright, and *perfectly clean*, is dipped into the boiling solution, which may be most conveniently done by placing it in a small perforated copper-ladle or wire-colander made for the purpose: the surface of the medal becomes at first black or dark-blue, and then (in about 5 minutes) acquires the desired brown tint; it must then be instantly withdrawn, (otherwise it changes colour,) and washed in a stream of water so as perfectly to remove all soluble matters from its surface; and lastly, very carefully wiped and dried. The medal is generally perfected by afterwards giving it one gentle pinch between the dies, in the coining-press. When there are many medals, each must be done separately, as they must not be allowed to touch each other, and care should be taken to rest them upon as few points of contact as possible. The bronzing-liquid also must not be suffered to concentrate by evaporation, but must be diluted if necessary, so as to keep it in a proper state, and especially to avoid all appearance of a white precipitation in it. It is better that the process should be too slowly than too rapidly effected. Medals and voltatypes may also be bronzed by covering their surface with plumbago, heating them to dull redness, and then brushing the surface till it acquires the desired tint.

Native Oxide of Copper, or *Ruby Copper*, is of a red or steel-gray colour, soft and brittle, and occurs massive, and crystallized in octoëdra, dodecaëdra, and cubes. Its specific gravity is 5.8 to 6. There is a beautiful variety in fine *capillary* crystals; and another, which is compact and earthy, called *Tile Ore*. Cornwall abounds in fine specimens of this ore.

PROTOXIDE OF COPPER ($Cu + O$) or Cu .—When copper is exposed to heat and air, its surface tarnishes, acquiring a yellow and then a violet colour, and at a high temperature black scales form upon it, which are thrown off on plunging it into water, or which fly off as it cools, in consequence of the rapid contraction of the metal. When these scales are reduced to a fine powder, and stirred in contact of air at a red heat, they yield the protoxide of copper. When nitrate of copper is exposed to heat gradually raised to redness, it fuses and is decomposed, and ultimately this oxide remains.

Protoxide of copper is black, or bluish, or brownish-black: its specific gravity is 6·4. Before the blowpipe, it fuses when intensely heated by the tip of the flame, upon charcoal: by the interior of the flame it readily affords a globule of metal. It is very easily decomposed at a dull red-heat, by hydrogen and by carbon; and consequently also by organic substances: hence its use in organic analysis; it is very hygrometric, and hence if weighed whilst hot, it generally augments in weight after cooling in consequence of the absorption of aerial moisture. It is insoluble in water, but it dissolves in, or combines with, the greater number of the acids, and is the basis of all the common salts of copper. When alkalis are dropped into its solutions, they throw it down as a bulky blue *hydrate*, which, however, is not permanent at a boiling heat, but becomes black and anhydrous. This oxide of copper is not soluble in the liquid fixed alkalis; but when carbonate of potassa or of soda are fused with it, it expels carbonic acid, and combines to form a blue or green compound. Its combination with ammonia will presently be noticed. It communicates a green, and sometimes a blue tint to vitreous compounds; and Sir H. Davy has shown that it is the basis of certain colours used by the ancients, which had been supposed to contain cobalt. (*Phil. Trans.*, 1815.) It consists of

	Proust:			Berzelius.		Gay Lussac.
Copper	1	32	80	80	80·13	80·28
Oxygen	1	8	20	20	19·87	19·72
Protoxide of copper	1	40	100	100	100·00	100·00

This oxide is sometimes considered as a *deutoxide* ($Cu + 2O$), and the dioxide as a *protoxide*: in this case 64 becomes the equivalent of copper. Gmelin and Berzelius, however, regard the salifiable oxide as the *protoxide*, or as constituted of 1 atom of copper and 1 of oxygen: Turner also has adopted this view, and urges in favour of it, 1. That the general characters of a suboxide belong to the red oxide; 2. That the equivalent of copper deduced from its specific heat (p. 163) is 32; and, 3. That the salts of the black oxide of copper are isomorphous with those of the protoxide of iron; which gives a strong presumption that those oxides possess the same atomic constitution. To these arguments it may be added, that the electro-chemical equivalent of copper appears to be 32.

HYDRATED PROTOXIDE OF COPPER, as thrown down from a solution of sulphate of copper by potassa or soda, is at first of an agreeable blue colour, but this soon changes to green, especially if it be dried; when it is used as a pigment, or colour for paper-staining, it is rendered more permanent by mixing it with glue or size, and chalk or alumina are also

généralement ajouté: il however soon acquires a green tinge. Dumas gives the following process for preparing a blue colour with this hydrate: 6 parts of sulphate of copper and 3 parts of chloride of calcium are dissolved in separate portions of water; the solutions are then mixed, and when the sulphate of lime has subsided the solution of chloride of copper is poured off and mixed with cream of lime, containing $1\frac{1}{2}$ parts of quicklime: the mixture is well agitated, and the greenish precipitate which falls, and which is an oxichloride of copper, being well drained, is ground up with a fourth part of lime and a fourth part of potash of commerce, so as to form a mixture of proper consistency. When this paste is put into bottles, a fourth part of sal-ammoniac and half a part of sulphate of copper are added to improve the colour, which however cannot be depended on, as it is apt to become green when dry, so that it is generally sold in the form of paste, to avoid the risk of desiccation.

COPPER AND CHLORINE.—Gaseous chlorine acts upon copper with great energy, and produces *two* chlorides; the one a comparatively fixed fusible substance, which is the *dichloride*: the other a yellow substance, which is a *protochloride*.

DICHLORIDE OF COPPER ($2Cu + C$) was first described by Boyle in 1666, under the name of *Rosin of Copper*. It was afterwards examined by Proust, who called it *White Muriate of Copper*. (*Ann. de Chimie*, xxviii. 218.) It may be obtained by exposing copper-filings to the action of chlorine not in excess: or by evaporating the solution of dioxide of copper in hydrochloric acid, and heating the residue in a vessel with a very small orifice; or by heating the protochloride in the same way. It is also the residue of the distillation of a mixture of 2 parts of corrosive sublimate and 1 of copper-filings. When protochloride of tin is added to any of the soluble salts of copper, or when copper-filings and the protoxide are digested in hydrochloric acid, this dichloride is also formed. It is insoluble in water, but soluble in hydrochloric acid, from which potassa throws down the hydrated dioxide. When water is added to its hydrochloric solution, it is thrown down in the form of a white granular hydrate: its colour varies, being generally dark-brown; but if fused and slowly cooled, it is yellow, translucent, and crystalline: it must be preserved out of contact of air. It consists of

					J. Davy.	
Copper	.	.	.	2	64	64
Chlorine	.	.	.	1	36	36
<hr/>					<hr/>	
Dichloride of copper				1	100	100

HYDRATED DICHLORIDE OF COPPER. SUBMURIATE OF COPPER.—When moistened dichloride of copper is exposed to air it acquires a greenish white colour, and becomes converted into a compound of chloride and oxide of copper, which has been termed *Submuriate of copper*, or *Brunswick green*; the same compound may be formed by adding hydrated oxide of copper to a solution of the chloride; or by exposing to the atmosphere slips of copper partially immersed in hydrochloric acid. This compound consists, according to John Davy, of 4 atoms of protoxide of copper, 1 of hydrochloric acid, and 3 of water.

CHLORIDE OF COPPER. PROTOCHLORIDE OF COPPER ($Cu + C$) may be formed by dissolving protoxide of copper in hydrochloric acid, and evaporating to dryness by a heat below 400° . Dumas obtains it by decomposing sulphate of copper by chloride of calcium: the sulphate of lime is separated by filtration, the solution evaporated to the consistence of syrup and mixed with alcohol, which dissolves the chloride without touching the sulphate.

Protochloride of copper is brown or yellowish when dry and anhydrous, but becomes blue by exposure to air; it is soluble in water and alcohol and very difficultly crystallizable. Exposed to a red heat in a tube with a very small orifice, gaseous chlorine is expelled, and it becomes a dichloride. It readily absorbs gaseous ammonia to the amount of 56 per cent., and forms a blue pulverulent mass. When it is decomposed by potassa not added in excess, and only so as partially to decompose it, a green oxichloride is thrown down, being, according to Dumas, identical with the native subchloride of copper. This chloride consists of

					J. Davy.	
"	Copper	1	32	47	47	
"	Chlorine	1	36	53	53	
<hr/>						
	Protochloride of copper	1	68	100	100	

OXICHLORIDE OF COPPER is found *native* in Peru and Chili, sometimes in the form of green sand, and sometimes massive and crystallized. The *green sand* was found in the river Lipas, in the desert of Atacama, separating Peru from Chili; hence mineralogists have termed this variety *Atacamite*. Chloride of copper has also been found upon some of the lavas of Vesuvius. The primitive form of this substance is an octoëdron. It is of a deep-green colour, and contains, according to Dr. Davy's analysis, 73 of oxide of copper, 16.2 of hydrochloric acid, and 10.8 of water; but, according to Dumas,

Protoxide of copper	3	120	53.5
Protochloride of copper	1	68	30.5
Water	4	36	16.0
<hr/>			
Native oxichloride of copper	1	224	100.0

CHLORATE OF COPPER ($Cu + C'$) is a blue-green deliquescent salt, difficultly crystallizable, formed by dissolving oxide of copper in chloric acid. A piece of paper dipped into its solution, burns with a remarkable green flame. (VAUQUELIN.) This salt is formed, according to Chenevix, by passing chlorine through a mixture of oxide of copper and water.

SUBIODIDE OF COPPER. DINIODIDE OF COPPER. ($2Cu + i$).—When iodide of potassium is added to a solution of the protosulphates of copper and iron, both in crystals, in the ratio of 1 to $2\frac{1}{4}$, the protoxide of iron takes the oxygen of the oxide of copper, and the iodine the metallic copper, with which it forms a white precipitate of the diniodide; it may be dried in close vessels. (TURNER.)

PROTIODIDE OF COPPER.—When iodide of potassium is added to a salt of protoxide of copper, iodine is set free, and a subiodide falls; the true protiodide ($Cu + i$) has not yet been examined.

DIBROMIDE OF COPPER. ($2cu + b.$)—Copper presents the same phenomena with bromine as with chlorine; the dibromide is insoluble in water, but soluble without decomposition in hydrochloric acid: sulphuric acid has no action on it. Heated in a tube it is not decomposed, but in the air it gives off vapours which colour flame green, and oxide of copper remains. Ammonia dissolves it and yields a crystallizable ammonio-bromide.

PROTOBROMIDE OF COPPER ($cu + b$) is formed by dissolving protoxide of copper in hydrobromic acid; the solution is green, but becomes brown by evaporation, and yields acicular crystals extremely deliquescent. Evaporated to dryness, it acquires a gray metallic lustre like plumbago. (SERULLAS.)

IODATE OF COPPER. ($Cu + i.$)—When solution of iodate of potassa is added to solutions of copper, an insoluble *iodate of copper* is thrown down.

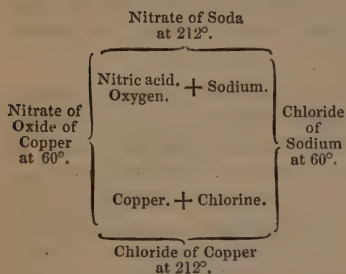
FLUORIDE OF COPPER.—When hydrated dioxide of copper is added to hydrofluoric acid, and evaporated out of the contact of air, a fusible compound of a black colour while hot, but becoming red as it cools, is obtained, which is a *difluoride of copper*. It forms a dark solution in hydrofluoric acid, and is precipitated white by water, but becomes red when collected upon a filter. When carbonate of copper is dissolved in hydrofluoric acid, carbonic acid is evolved, and an insoluble compound is at length formed, the properties of which are not very explicitly detailed by Berzelius, who alone has examined this and the preceding compound.

NITRATE OF COPPER. ($Cu + n.$)—Nitric acid diluted with 3 parts of water rapidly oxidizes copper, evolving nitric oxide, and ultimately forming a bright-blue solution, which affords deliquescent prismatic crystals on evaporation, of a fine blue colour, caustic, and very soluble in water and in alcohol. They contain a considerable portion of water, which causes them to liquify at a temperature below 212° . At a higher temperature they lose water and acid, becoming a *subnitrate*, and are entirely decomposed at a red heat. The anhydrous nitrate of copper consists of

Oxide of copper	1	40	42.6
Nitric acid	1	54	57.4
Anhydrous nitrate of copper	1		94		100.0

The quantity of water contained in the prismatic nitrate amounts, according to Graham, to 3 atoms, but it sometimes crystallizes in rhomboidal plates, which contain 6 atoms of water. Potassa forms, in the solution of this nitrate, a bulky blue precipitate of *hydrated oxide of copper*, which, as already observed, when boiled in potassa or soda, becomes black from the loss of its combined water. When nitrate of copper is coarsely powdered, sprinkled with a little water, and quickly rolled up in a sheet of tin-foil, there is great heat produced, nitrous gas is rapidly evolved, and the metal often takes fire. (HIGGINS, *Phil. Transactions*, LXIII.) If ammonia be added to solution of nitrate of copper, it occasions a precipitate of the hydrated oxide; but if it be added in excess, the precipitate

is redissolved, and a triple *ammonio-nitrate of copper* is produced. It is a soluble crystallizable salt, which detonates slightly when heated. It is best formed by passing ammoniacal gas into a saturated solution of nitrate of copper. According to Kane it is anhydrous, and contains 1 atom of nitric acid, 1 of oxide of copper, and 2 of ammonia. Graham represents it as an ammoniated nitrate of cuprammonium, by the formula $(A + Cu) + (A + N')$, that is, as a double salt formed of 1 atom of cuprate of ammonia and 1 of nitrate of ammonia. When solutions of nitrate of copper and chloride of sodium are mixed at common temperatures, the mixture remains blue, and no decomposition ensues; but on raising its temperature to 212° , it becomes of a vivid green, indicating the formation of chloride of copper; on again cooling, the blue colour returns, and this interchange of elements may be repeated any number of times.



On evaporating the mixed solutions to a small bulk, chloride of copper is permanently formed, and rhomboidal crystals of nitrate of soda are deposited. Mr. Alfred Taylor, to whom I am indebted for this experiment, illustrates it by the annexed diagram; the vertical brackets pointing to the state of the salts at 60° , and the horizontal to that at 212° .

SUBNITRATE OF COPPER.—When caustic potassa, not in excess, is added to solution of nitrate of copper, or when the salt is carefully heated so as to expel part of its acid, and the residue washed, there remains an insoluble pale-green salt, composed of

				Berzelius.	Proust.
Oxide of copper	5	200	66.89	66.0	67
Nitric acid	1	54	18.06	18.9	16
Water	5	45	15.05	15.1	17
<hr/>					
Subnitrate of copper	1	299	100.00	100.0	100

According to Graham, the green insoluble subsalt, produced by exposing the neutral nitrate to a temperature between 150° and 600° , is a *trinitrate*, and contains 3 atoms of oxide of copper, 1 of acid, and 1 of water. "When oxide of copper is drenched with the most concentrated nitric acid ($N + 5O + q$) it is this subsalt, singular as it may appear, which is formed, even when the acid is in great excess; the reason seems to be that the nitrate of water being deficient in constitutional water, assumes 3 atoms of oxide of copper in its place."

AMMONIURET OF OXIDE OF COPPER. CUPRATE OF AMMONIA.—If oxide of copper be digested in ammonia it is dissolved, forming a bright-blue solution, which, by careful evaporation, affords dark blue crystals. A mixture of lime, sal-ammoniac, and water, placed in a copper vessel, or mixed with oxide of copper, also affords a deep blue liquor in consequence of the action of the ammonia on the oxide of copper. This solution is the *Aqua Sapphirina* of old pharmacy.

The dioxide of copper also dissolves in ammonia, but the solution is colourless; if it be exposed to air it becomes blue. This may be well shown by filling a tall glass with liquid ammonia, and adding a few drops of a solution of the dichloride of copper; the liquid presently acquires a blue colour upon the surface, but remains for some time colourless below. If clean copper-filings be digested in a well-stopped phial with liquid ammonia, a colourless solution of the dioxide is also formed, which becomes blue on momentary exposure to air. When these ammoniacal solutions are very copiously diluted, or when potassa is added to them, they are decomposed, and hydrated oxide of copper falls.

COPPER AND SULPHUR. DISULPHURET OF COPPER, ($2\text{Cu} + \text{S}_2$) may be formed artificially, by heating a mixture of copper-filings and sulphur: as soon as the latter melts, a violent action ensues, the copper becomes red-hot, and a black brittle compound is formed. It may also be produced by fusing sulphur with oxide of copper. It is soluble in hydrochloric acid, with the evolution of sulphuretted hydrogen; and in nitric acid, with the separation of sulphur. It consists of

				Berzelius.	Vauquelin.
Copper	2	64	80	79.73	78.69
Sulphur	1	16	20	20.27	21.31
Disulphuret of copper	1	80	100	100.00	100.00

Native Disulphuret of Copper. Vitreous Copper.—This ore of copper is chiefly found in primitive countries. In England, it occurs in great beauty, crystallized and massive, in Cornwall, and in Yorkshire. Its colour is gray; its lustre shining and metallic; and it yields easily to the knife. Its primitive form is a six-sided prism, which passes into the dodecaëdron with triangular faces, and its various modifications. A variety of *black sulphuret of copper*, containing iron and arsenic, has been described by Messrs. W. and R. Phillips, under the name of *Tennantite*; its most ordinary form is the rhomboidal dodecaëdron, either perfect or variously modified. (*Quarterly Journal of Science and Arts*, vii. 95.)

SULPHURET OF COPPER. ($\text{Cu} + \text{S}$).—This compound cannot be formed by fusion, but it is thrown down when sulphuretted hydrogen is passed through a solution of protoxide of copper: the precipitate is at first brown, but becomes black, and when dried assumes a greenish hue. In this state it reddens moistened litmus paper, and when heated gives off a little water and sulphurous acid, and sulphur, and the disulphuret remains. It is insoluble in potassa, and in the sulphuretted alkalis. It consists of

Copper	1	32	66.67
Sulphur	1	16	33.33
Protosulphuret of copper	1	48	100.00

FERROSULPHURETS OF COPPER.—*Copper Pyrites, or Yellow Copper Ore*, is the most important and generally occurring ore, from which the largest proportion of the copper of commerce is derived; it occurs in a variety of forms, its primitive crystal being the regular tetraëdron. The British mines are very productive of this ore. A beautiful iridescent variety occurs in the Ecton mine in Staffordshire. The composition of

the different varieties of copper pyrites, appears in all cases to be sulphur, copper, and iron. The *variegated copper* Mr. Phillips regards as a compound of 1 proportional of sulphuret of iron, 2 proportionals of sulphuret of copper. (*Ann. of Phil.*, iii. 87.)

The *yellow copper ore* is also a double sulphuret of iron and copper: and, omitting the small portion of lead and arsenic with which it is usually contaminated, it may be considered as a compound of 2 proportionals of sulphuret of iron, 1 proportional of sulphuret of copper. (PHILLIPS, *Ann. of Phil.*, iii. 301.)

REDUCTION OF COPPER ORES.—The following is an outline of the process by which these ores of copper are reduced, as carried on upon a very large scale near Swansea, where the chief part of the Cornish ores are brought to the state of metal. The ore, having been picked and broken, is heated in a reverberatory furnace, by which arsenic and sulphur are driven off. It is then transferred to a smaller reverberatory, where it is fused, and the slag which separates, being occasionally removed, is cast into oblong masses which are used as a substitute for bricks. The impure metal collected at the bottom of the furnace is granulated by letting it run into water: it is afterwards remelted and granulated two or three times successively, in order further to separate impurities, which are chiefly sulphur, iron, and arsenic, and ultimately cast into oblong pieces called *pigs*, which are broken up, roasted, and melted with a portion of charcoal in the refining furnace. Malleability is here conferred upon the copper, and its texture improved, by stirring the metal with a pole of green wood, generally birch, which causes great ebullition and agitation; assays are occasionally taken out, and the metal, originally crystalline and granular when cold, now becomes fine and close, so as to assume a silky polish when the assays are half cut through and broken. The metal is now cast into cakes about 12 inches wide by 18 in length. The whole process of refining the copper, and toughening it by *poling*, requires much care and attention; and if it be over-poled, the metal is even rendered more brittle than in its original state. The effect of *poling* has not been satisfactorily explained; it may consist in the separation of a small portion of oxide of copper, and the effect of over-poling may possibly depend upon the combination of the copper with a portion of carbon. Copper for brass-making is granulated by pouring the metal through a perforated ladle into water; when this is warm the copper assumes a rounded form, and is called *bean-shot*; but if a constant supply of cold water is kept up it becomes ragged, and is called *feathered-shot*. Another form into which copper is cast, chiefly for exports to the East Indies, is in pieces of the length of six inches, and weighing about 8 ounces each: the copper is dropped from the moulds, immediately on its becoming solid, into a cistern of cold water, and thus, by a slight oxidation of the metal, the sticks acquire a rich red colour on the surface. This is called *Japan copper*. A large quantity of copper is rolled into sheets and sheathings, both for export and home consumption. (For an excellent account of the reduction of copper, as carried on this country, see Mr. Vivian's paper, *Ann. of Phil.*, N.S., v. 113.)

HYOSULPHITE OF COPPER was formed by Herschel by mixing hypo-

sulphite of potassa with sulphate of copper. It is colourless; of an intensely sweet taste; and, provided air be excluded, it is not turned blue by ammonia. (*Edin. Phil. Journ.*, i. 24.)

SULPHITE OF COPPER ($\text{Cu} + \text{S}$) may be obtained by passing sulphurous acid into water, through which oxide of copper is diffused. Small red crystals are formed, composed of oxide of copper and sulphurous acid. When sulphite of potassa is added to nitrate of copper a precipitate falls, which assumes the form of red and yellow crystals. The former are sulphite of copper; the latter a triple *sulphite of potassa and copper*. (CHEVREUL, *Ann. de Chim.*, LXXXiii. 181.)

HYPOSULPHATE OF COPPER ($\text{Cu} + \text{S}'$) is formed by adding a solution of sulphate of copper to one of hyposulphate of baryta; it crystallizes in small prisms, very soluble in water, but insoluble in alcohol, and slightly efflorescent. When a little ammonia is added to its solution a green powder falls, which is a *subhyposulphate*, composed of 4 atoms of oxide, 1 of acid, and 4 of water. The crystallized neutral hyposulphate contains

Oxide of copper	1	40	27.03	Heeren.
Hyposulphuric acid	1	72	48.65	26.43
Water	4	36	24.32	48.10
Crystallized hyposulphate of copper	1	148	100.00	25.47
				100.00

SULPHATE OF COPPER. ROMAN VITRIOL. BLUE VITRIOL. ($\text{Cu} + \text{S}/$.)
—This salt is easily formed by dissolving recently precipitated oxide of copper in diluted sulphuric acid, or by exposing copper to the joint action of moderately dilute sulphuric acid and air. It may also be formed by boiling copper in sulphuric acid, either concentrated or diluted with half its bulk of water, a process which furnishes abundance of sulphurous acid, but which is not generally had recourse to, to produce sulphate of copper. It is made upon a large scale, by exposing roasted sulphuret of copper to air and moisture, and thus obtained is impure, containing iron, and often zinc: it is the common *blue vitriol* of commerce. It is also obtained in large quantities, and very pure, in certain processes afterwards to be described for refining gold and silver; and it is occasionally prepared by dissolving in sulphuric acid an oxichloride of copper made for the purpose, by exposing sheet copper to the joint action of air and hydrochloric acid.

Sulphate of copper forms rhomboidal crystals, which are sometimes of very large dimensions, and of a beautiful sapphire-blue colour, doubly refractive, and liable to slight efflorescence in a moderately dry atmosphere: they are soluble in 4 parts of cold and 2 of boiling water: the density of this salt is 2.20. It has a peculiarly nauseous metallic taste. When heated to 212° it loses 4 atoms of its water of crystallization, and crumbles down into a pale blue powder: heated to 400° the whole of its water is expelled, and it becomes white: in this state it slowly re-absorbs water from the air, and regains its blue colour; or if sprinkled with water much heat is evolved, and the salt crumbles down into a blue hydrate: by a continued high-red or white heat, sulphuric acid (anhydrous) is evolved, and oxide of copper remains. This

salt is the *Vitriol*, or *Salt of Venus*, of the alchymists. It is much used in the arts as a source of several blue and green colours. It is also employed by dyers and calico-printers, and is an ingredient in some kinds of writing ink. It has also been used to prevent smut in corn, by steeping the grain in a dilute solution of the salt (*Quart. Journ.*, xvi. 156); and minute quantities of it are occasionally added to bread, (in Paris especially,) to improve its colour and quality. (*Archives Gén. de Médecine*, xxi. 145.) In medicine it is resorted to as a powerful emetic; and, in very minute doses, as a tonic. It is also a valuable external application as an astringent, or when undiluted, as a styptic and caustic. It may be employed to prevent *dry rot* by steeping timber or planks in its solution; and it is a powerful preservative of animal substances, which, when imbued with it, and dried, remain unaltered. The waters of copper-mines often hold it in solution, and, when decomposed by immersing in them pieces of iron, yield precipitated metallic copper, (copper of cementation.) The precipitation of metallic copper during the electro-chemical decomposition of an aqueous solution of this salt, and its application in the beautiful process for obtaining copies of medals and other works of art, has already been alluded to (p. 308).

The elements of sulphate of copper in its anhydrous state are

	Berzelius.			
Oxide of copper	1	40	50	50·9
Sulphuric acid	1	40	50	49·1
<hr/>				
Anhydrous sulphate of copper	1	80	100	100·0

The common rhomboidal crystals contain

	Proust.			Berzelius.
Oxide of copper	1	40	32	32·13
Sulphuric acid	1	40	32	31·57
Water	5	45	36	36·30
<hr/>				
Crystals of sulphate of copper	1	125	100	100·00

When a solution of sulphate of copper is made to crystallize in a warm place, prismatic crystals of a green colour are sometimes obtained, which only contain 1 atom of water of crystallization. (THOMSON.)

DISULPHATE OF COPPER. ($2\text{Cu} + \text{S}'$).—When a solution of sulphate of copper is boiled for a long time with a quantity of oxide of copper equal to that contained in the salt, the solution at last becomes colourless, and a green powder is deposited, containing all the oxide of copper, and all the sulphuric acid: it is therefore a disulphate. (THOMSON.)

TRISULPHATE OF COPPER.—When a solution of sulphate of copper is precipitated by a small addition of potassa, a green, tasteless, insoluble powder falls, composed of

	Berzelius.			
Oxide of copper	3	120	64·17	64·22
Sulphuric acid	1	40	21·39	21·28
Water	3	27	14·44	14·50
<hr/>				
Trisulphate of copper	1	187	100·00	100·00

TETRASULPHATE OF COPPER.—When solutions of sulphate of potassa and sulphate of copper are boiled together, a green powder falls, which, if

boiled in repeated portions of water, leaves an insoluble residue, composed according to the analysis of Brunnen (*Poggend., Ann.*, xv.) of 4 atoms of oxide of copper, 1 of sulphuric acid, and 3 of water. The blueish-green precipitate which falls when ammonia or potassa are added in moderate quantity to sulphate of copper, contains, according to Kane and Graham, 4 atoms of oxide of copper, 1 of sulphuric acid, and 4 of water. By a larger quantity of potassa, Dr. Kane precipitated a clear grass-green subsulphate, containing 8 atoms of oxide of copper, 1 of sulphuric acid, and 12 of water; this salt loses exactly half its water at 300°. (GRAHAM, *Elem. of Chem.*, 584; KANE, *Trans. Royal Irish Acad.*, xix.)

AMMONIO-SULPHATE OF COPPER.—When a mixed solution of sulphate of copper and sulphate of ammonia is evaporated, blue soluble crystals are obtained, composed of

	Berzelius.				Mitscherlich.			
Ammonia . . .	1	17	8.5		1	17	8.14	
Oxide of copper .	1	40	20.0		1	40	19.14	
Sulphuric acid .	2	80	40.0		2	80	38.27	
Water . . .	7	63	31.5		8	72	34.45	
	1	200	100.0		1	209	100.00	

AMMONIO-SUBSULPHATE OF COPPER.—When a solution of sulphate of copper is supersaturated by ammonia, so as to redissolve the precipitated oxide, dark-blue crystals may be obtained by very careful evaporation, forming the *cuprum ammoniacale* of pharmacy. When ammoniacal gas is conducted into a hot saturated solution of the sulphate, this salt is also obtained in indigo-blue crystals. Exposed for a long time to air they lose ammonia, and crumble down into a green powder: (a mixture of sulphate of ammonia and carbonate of copper.) They are soluble in 1.5 cold water, and insoluble in alcohol; the aqueous solution, largely diluted, deposits trisulphate of copper. The crystals consist of

	Berzelius.			Brandes.	
Ammonia	2	34	27.64	26.40	21.42
Oxide of copper	1	40	32.52	34.00	33.08
Sulphuric acid	1	40	32.52	32.25	31.75
Water	1	9	7.32	7.35	13.35
Crystals of subsulphate of } ammonia and copper }	1	123	100.00	100.00	99.60

At 390° these crystals lose 1 atom of ammonia and 1 atom of water, and are converted into a green powder ($\text{Cu} + \text{A} + \text{S}'$). (KANE.) Heated to 500° the whole of the ammonia is expelled and sulphate of copper remains.

Anhydrous sulphate of copper rapidly absorbs ammoniacal gas, acquiring a deep blue colour, increasing greatly in bulk and evolving heat. 100 parts absorb 53.20 of ammonia. (H. ROSE, *Ann. de Ch. et Ph.*, lxii. 311.)

SULPHATE OF COPPER AND POTASSA is a double salt, formed by digesting hydrated oxide of copper in bisulphate of potassa. It crystallizes in rhomboids of a pale blue colour, and consists of 1 atom of sulphate of potassa, 1 of sulphate of copper, and 6 of water.

PHOSPHURET OF COPPER ($Cu + p$) is most easily made by dropping pieces of phosphorus on red-hot copper-wire. It is more fusible than copper. Its specific gravity is 7.12. Pelletier found it composed of 100 copper + 20 phosphorus.

Neither the *Hypophosphite* nor *Phosphite* of copper have been examined.

PHOSPHATE OF COPPER.—When solutions of sulphate of copper and phosphate of soda are mixed, a bluish-green insoluble powder falls, which is probably a *hydrated subphosphate*, composed, according to Chenevix (*Phil. Trans.*, 1801), of 49.5 oxide, 35 acid, 15.5 water.

Native Phosphate of Copper has been found near Cologne. It is of a green colour, and forms small rhomboidal crystals. A specimen, analyzed by Mr. Lunn (*Ann. of Phil.*, iii. 182), afforded, phosphoric acid 21.687, peroxide of copper 62.847, water 15.454.

SELENIURET OF COPPER ($Cu + Se$) is formed by heating copper-filings with selenium: they act with intense ignition, and a black brittle compound results.

SELENITE OF COPPER.—When a hot solution of sulphate of copper is mixed with biselenite of ammonia, a precipitate falls, at first yellow, but which afterwards becomes greenish-blue and crystalline. When sulphate of copper is decomposed by selenite of ammonia, with excess of ammonia, a green *diselenite* is precipitated.

CARBURET OF COPPER.—The pale yellowish-red and fibrous copper, (overpoled,) appears to contain carbon. (VIVIAN, *Ann. of Phil.*, v. 121.)

CARBONATES OF COPPER.—A neutral carbonate of copper ($Cu + car'$) is unknown. When hot solutions of copper are precipitated by the carbonated fixed alkalis, a bulky *hydrated dicarbonate of copper*, of a green colour, falls: its tint is improved by repeated washing with boiling water. It is prepared as a pigment under the name of *mineral green*, or *green verditer*. When native, it is known under the name of *malachite*. It consists of

	Native.						Artificial.	
	Phillips.	Klaproth.	Vauquelin.	Berzelius.	Proust.			
Oxide of copper	2	80	72.07	72.2	70.5	70.00	71.70	69.5
Carbonic acid	1	22	19.82	18.5	18.0	21.25	19.73	25.0
Water	1	9	8.11	9.3	11.5	8.75	8.57	5.5
Hydrated subcarbonate of copper }	1	111	100.00	100.0	100.0	100.00	100.00	100.0

When it is long boiled in water, or when carefully heated, it becomes of a deep-brown colour, and *anhydrous*, consisting, in that state, which occurs *native*, of

	Thomson.			
Oxide of copper	2	80	78.43	78.42
Carbonic acid	1	22	21.57	21.58
Anhydrous subcarbonate of copper	1	102	100.00	100.00

When a cold dilute solution of sulphate of copper is decomposed by carbonate of potassa, a blue precipitate falls, which, by careful management during drying, retains its blue colour, and is known in commerce

under the name of *blue verditer**. It generally contains a little lime. (PHILLIPS, *Quart. Jour.*, iv. 277.) It differs from the green carbonate, according to Colin and Tallefert (*Ann. de Ch. et Ph.*, xii. 62), in containing more water. It appears to be a compound of

	Phillips.				Klaproth. Vauquelin. Pelletier.			
	Native.		Artificial.		Native.		Artificial.	
Oxide of copper	3	120	69.37	69.08	67.6	70	68.75	59.7
Carbonic acid	2	44	25.43	25.46	24.1	24	25.00	30.0
Water	1	9	5.20	5.46	5.9	6	6.25	3.3
Impurities					2.4			7.0

NATIVE CARBONATES OF COPPER.—*Malachite*, or the *green hydrous carbonate*, is found in various forms, but never regularly crystallized, the octoëdral variety being a pseudo-crystal derived from the decomposition of the red oxide. This mineral occurs in the greatest beauty in the Uralian Mountains of Siberia; it is rarely found in Cornwall. It is of various shades of green, and often cut into small slabs, or used as beads and brooch-stones. The pulverulent variety has been termed *chrysocolla* and *mountain-green*. The *blue carbonate* is found in great perfection at Chessy, near Lyons; also in Bohemia, Saxony, &c. It occurs crystallized in rhomboids and imperfect octoëdra; it is also found in small globular masses; massive, and earthy. The earthy variety is sometimes called *copper-azure* or *mountain-blue*. The *Diopase*, or *Copper Emerald* is a very rare mineral, hitherto found only in Siberia, associated with malachite. It consists, according to Lowitz, of oxide of copper, silica, and water. Some of the varieties of malachite appear to contain a silicate of copper.

BORATE OF COPPER.—Solution of borax, poured into sulphate of copper, produces a bulky pale-green precipitate of *borate of copper*.

CYANURETS OF COPPER.—Hydrocyanic acid and hydrocyanate of potassa throw down a white curdy precipitate in the solution of dichloride of copper. A similar compound is obtained by the action of dilute hydrocyanic acid upon hydrated dioxide of copper: it is soluble in ammonia, and the solution is colourless; it is also soluble in hydrochloric acid and precipitated by dilution, and by potassa: it combines with other metallic cyanurets, forming a class of *cuprocyanurets*. When hydrated oxide or carbonate of copper is digested in dilute hydrocyanic acid, a yellow powder is formed, insoluble in water, soluble in hydrochloric acid, and again precipitable by dilution.

CUPROCYANURET OF POTASSIUM.—Cyanuret of copper, digested in a solution of cyanuret of potassium, yields a yellow solution, from which small yellow transparent prismatic crystals may be obtained, of a bitter

* There is a very inferior pigment, also called *verditer*, which is a mixture of subsulphate of copper and chalk. According to Pelletier, a good verditer may be obtained as follows:—Add a sufficient quantity of lime to nitrate of copper to throw down the hydrated oxide; it gives a greenish precipitate, that is

to be washed and nearly dried upon a strainer; then incorporate with it from 8 to 10 per cent. of fresh lime, which will give it a blue colour, and dry it carefully. According to Mr. Chenevix, the alkaline carbonates dissolve a portion of the peroxide of copper, and form double salts.

metallic taste. This salt is not altered by the alkalis, but acids precipitate cyanuret of copper from it, which excess of acid afterwards dissolves with the evolution of hydrocyanic acid. (ITTNER.) According to L. GMELIN (*Handbuch*, Art. KUPFER) these crystals, if obtained from oxide (and not from dioxide) of copper, are a *cupro-dicyanuret* of potassium; for during the solution of oxide of copper in cyanuret of potassium, cyanogen is evolved, and the solution yields a white curdy precipitate of dicyanuret of copper on the addition of hydrochloric acid. When a solution of this cuprocyanuret is added to other metallic solutions, an interchange ensues between the potassium and the metal in the solution, and double cyanurets are formed, in which one of the metals is always copper: the precipitate with *gold* is green; with *silver*, dark-brown; with protosalts of *iron*, greenish-yellow; with the persalts of iron the precipitate is only a mixture of cyanuret of copper with peroxide of iron; with *lead*, pale-green; with *zinc*, *bismuth*, and *manganese*, pale-yellow. Acids decompose these precipitates, dissolving them, and evolving hydrocyanic acid; the compound with iron yields protocyanuret of iron, which becomes blue by exposure to air. All the salts of *tin* yield mere mixtures of cyanuret of copper and oxide of tin: the relative proportion of the copper to the other metals, in these compounds, has not been accurately determined. (BERZELIUS.)

FERROCYANURET OF COPPER is thrown down by ferrocyanuret of potassium, from the solutions of oxide of copper, in the form of a rich-brown powder, which has been used as a pigment; it is partially soluble in ammonia, insoluble in acids, and decomposed by caustic potassa. Cold concentrated sulphuric acid whitens it, but, on the addition of water, it again becomes brown. Ferrocyanuret of potassium is so delicate a test of the salts of copper, that it will distinctly detect 1 part of that metal in 60,000 of the solution.

SULPHOCYANURET OF COPPER is formed by adding a solution of protosulphate of iron to a mixture of sulphate of copper and sulphocyanuret of potassium: it falls as a white granular precipitate, insoluble in water: its formula is (*cu + sulcy*). (LIEBIG.)

ALLOYS OF COPPER.—Many of these compounds are of great use in the arts, especially those with zinc and tin, and with silver and gold; of these, the two latter will be noticed under those metals. The alloys of copper with *potassium* and *sodium* have not been particularly examined. Davy formed them, and ascertained that they decompose water. *Manganese* was combined with copper by Bergman, and the properties of the alloy were examined by Gmelin. (*Göttingen Commentaries*, 1787.) *Iron* and copper combine with difficulty: 100 parts of gray cast-iron and 5 of copper yield a very hard alloy, of which Rinmann has proposed to make anvils. With *zinc* and *tin* copper forms brass and bronze. With *cadmium*, the alloy is brittle and harsh; it is decomposed by keeping it in fusion, when the cadmium volatilizes. The alloy of copper and *cobalt* has not been examined. With *nickel*, copper yields pakfong and German silver (see *Nickel*, p. 810). Dumas gives the following view of the composition of different pakfongs.

	For spoons and forks.	For knife handles and snuffers.	For lamination.	For articles which require soldering.	White, but harsh and hard.	Chinese paktong.
Copper	50	55	60	57	53	40·4
Nickel	25	22	20	20	22	31·6
Zinc	25	23	20	20	23	25·4
Lead	0	0	0	3	0	0·0
Iron	0	0	0	0	2	2·6
	100	100	100	100	100	100·0

German nickel is used by the manufacturers of paktong: it is broken up and mixed with the granulated copper and zinc, taking care that copper forms the upper and lower stratum in the crucible: the whole is covered with charcoal-powder and fused in a wind furnace; it is stirred and kept for some time in fusion, at the risk of evaporating part of the zinc. When the clippings and filings are remelted, 3 or 4 per cent. of zinc are added to compensate for volatilization.

BRASS.—In making this important alloy, the metals are usually united by mixing granulated copper with calamine and charcoal: the mixture is exposed to heat sufficient to reduce the calamine and melt the alloy, which is then cast into plates. The relative proportions of the two metals vary in the different kinds of brass; and some contain a little lead and tin. The composition of the principal varieties is shown in the following table:—

	For Turning.		For Gilding.		For Wire.	For Ham- mering.	For Fine Casting.	
Copper	61·6	65·8	63·7	82	66·5	70	91·2	91·7
Zinc	35·3	31·8	33·6	18	33·1	30	5·6	5·0
Lead	2·9	2·2	2·5	1	0·4	0	1·8	2·3
Tin	0·2	0·2	0·2	3	0·0	0	1·4	1·0
	100·0	100·0	100·0	104	100·0	100	100·0	100·0

Brass is very malleable and ductile when cold; and its colour and little liability to rust recommend it in preference to copper for many purposes of the arts: its specific gravity varies from 7·9 to 8·9, and exceeds the mean of its components, as shown by the following results. (DUMAS.)

	Copper.	Zinc.	Actual Density.	Calculated Density.
I.	70	30	8·443	8·390
II.	80	20	8·940	8·560

According to Regnault, the specific heat of a brass composed of 71 copper, 27·6 zinc, and 1·3 lead, and affording traces of tin, is 0·09391. (*Ann. de Ch. et Ph.*, LXXIII. 33.) According to Sage, a beautiful brass may be made by mixing 50 parts of oxide of copper, 100 of calamine, 400 of black flux, and 30 of charcoal-powder; melt these in a crucible till the blue flame is no longer seen round the cover; and, when cold, a button of brass is found at the bottom, of a golden colour, and weighing one-sixth more than the pure copper obtained from the above quantity of oxide. The presence of iron and of tin in brass should be carefully avoided, where they may interfere with its ductility or malleability.

Tutenag is said to be an alloy of copper, zinc, and a little iron; and *Tombac*, *Dutch Gold*, *Similor*, *Prince Rupert's Metal*, and *Pinchbeck*, are alloys containing more copper than exists in brass, and consequently

made by fusing various proportions of copper with brass. According to Wiegleb, *Manheim Gold* consists of 3 parts of copper and 1 of zinc. A little tin is sometimes added, which, though it may improve the colour, impairs the malleability of the alloy. An alloy of 576 parts of copper, 59 of tin, and 48 of brass, is equal to brass in hardness, and may be worked with the same facility; it was used by Mr. Bate for the new standard measures, as being less liable than brass to oxidizement. (*Phil. Trans.*, 1826.)

Speculum Metal is an alloy of copper and tin, with a little arsenic; about 6 copper, 2 tin, 1 arsenic. On this subject the reader is referred to Mr. Edwards's experiments. (*NICHOLSON'S Journal*, 4to., iii.) Mr. Little recommends 32 parts of best bar copper, 4 of brass pin-wire, $16\frac{1}{2}$ of tin, and $1\frac{1}{4}$ of arsenic. He first melts the brass, and adds about its weight of tin; when this is cold, the copper, previously fused with black flux, is added; then the remainder of the tin; and, lastly, the arsenic. This mixture is granulated, and again fused for casting.

BRONZE. BELL-METAL.—These are alloys of copper and tin; they are harder and more fusible, but less malleable, than copper. The specific gravity of bronze exceeds the mean of its component metals, when carefully hammered and free from air-blebs: but bronze castings are apt to be more or less porous and vesicular, unless considerable care and skill have been used in fusing and pouring the metal, and in the construction of the mould; and in large castings, owing to the gradual cooling of the mass, there is often a want of uniformity in the composition of different parts of it; that portion containing the least tin being the first to solidify, while the more fusible portion, to a certain extent separates, and is sometimes projected from the mould. The following table, from the experiments of Briche, shows the actual and calculated density of different alloys of copper and tin. (*Journ. des Mines*, v.)

Copper.	Tin.	Actual Density.	Calculated Density.	Difference.
100 . . .	4 . . .	8·79 . . .	8·74 . . .	0·05
100 . . .	6 . . .	8·78 . . .	8·71 . . .	0·07
100 . . .	8 . . .	8·76 . . .	8·68 . . .	0·08
100 . . .	10 . . .	8·76 . . .	8·66 . . .	0·10
100 . . .	12 . . .	8·80 . . .	8·63 . . .	0·17
100 . . .	14 . . .	8·81 . . .	8·61 . . .	0·20
100 . . .	16 . . .	8·87 . . .	8·60 . . .	0·27
100 . . .	33 . . .	8·83 . . .	8·43 . . .	0·40
100 . . .	100 . . .	8·79 . . .	8·05 . . .	0·74

In large bronze castings, such as statues, porosity and bubbles require carefully to be avoided; where they exist so as to deface the appearance of the work, they are sometimes filled up with substances which are only temporarily durable, or which, if metallic, give rise to electrical effects which time must render prejudicially evident: for this reason also, the different pieces of a large statue should be fused together, or united by bronze, and not by a mere fusible solder; and iron bars, and leaden junctions for the support or fixing of the work, should, upon the same principle, be avoided, as they are themselves liable, under such circumstances, to rapid corrosion, and this may affect the stability, or safety of the statue, independent of other influences.

When bronze is frequently remelted it gradually loses tin by oxidizement, so that in such cases fresh additions of tin may sometimes be requisite; and it is apparently this oxidizement of the tin which tends to deteriorate the texture of remelted bronzes, and renders them more subject to bubbles and porosity when recast, an effect which may be prevented by the action of carbonaceous fluxes, or by the operation of poling, as in the case of copper.

Tempering produces upon bronze an effect directly opposite to that upon steel; and in order to render bronze malleable, or fit for the coining press, it must be heated to redness and quenched in water: the alloy which thus acquires the greatest tenacity is that of 8 of copper and 1 of tin, and this is consequently preferable for medals; the advantage of bronze over copper for these purposes being hardness, and resistance to oxidizement; the former quality resists friction, and the latter has handed down to us the works of the ancients with little deterioration, though buried for ages in damp soil, or immersed in water: the small value of bronze, too, as compared with gold and silver, is another important consideration, as affecting the preservation of such works of art. The following are the component parts of the different bronzes and bell-metals in common use.

	For Coin and Medals.		Gongs and Cymbals.		Gun-metal. Statues and Large Castings.		Bell-metal.	
Copper	93	89	78	92	89	80	83	
Tin	7	11	22	8	11	10	17	
Zinc	0	0	0	0	0	6	0	
Lead	0	0	0	0	0	4	0	
	100	100	100	100	100	100	100	

The analysis of brass may be performed by solution in nitric acid; add considerable excess of solution of potassa, and boil, which will dissolve the oxide of zinc and leave that of copper; wash the latter, and dry and heat it to redness: 100 parts indicate 80 of copper. The zinc in the filtered alkaline solution may be precipitated by carbonate of soda, having previously added a small excess of hydrochloric acid; wash this precipitate, dry it, and expose it to a red heat; it is then oxide of zinc, 100 parts of which indicate 80 of metal. But as, in this process, the whole of the oxide of zinc is not easily removed by the alkaline solution, Mr. Keates recommends the following as a preferable operation:—Dissolve the brass in dilute nitric acid, evaporate to dryness, and redissolve in excess of dilute sulphuric acid; filter, to separate sulphate of lead, if any be present; dilute the solution, heat it to its boiling-point, and introduce three polished cylinders of iron, each about an inch long and a fourth of an inch diameter; continue the boiling till the solution becomes colourless, and when tested by a clean plate of iron shows no trace of copper. Filter the solution while hot, and wash the precipitated copper first with very dilute sulphuric acid, and afterwards with boiling water; dry it, and fuse it into a button in a crucible covered with charcoal-powder. Boil the filtered solution with the addition of some nitric acid to peroxidize the iron, and nearly neutralize by carbonate of soda; then add excess of ammonia, to throw down the peroxide of iron, which separate by filtration.

Add hydrochloric acid to the filtered ammoniacal solution, evaporate to dryness, and heat in a silver crucible to drive off hydrochlorate of ammonia; dissolve the residue in hydrochloric acid, and precipitate by excess of carbonate of soda; wash, dry, and ignite the precipitate, which reduces it to the state of oxide of zinc.

The analysis of alloys of tin and copper may be performed by digestion in nitric acid, which dissolves the copper and converts the tin into insoluble peroxide, which, when washed and dried, consists of 78.4 tin + 21.6 oxygen. The cupreous solution may be decomposed by potassa, and the pure peroxide of copper indicates the quantity of that metal, as in the analysis of brass.

Tinned Copper.—Vessels of copper used for culinary purposes are usually coated with tin, to prevent the food being contaminated with copper. Their interior surface is first cleaned, then rubbed over with sal-ammoniac. The vessel is then heated, a little pitch spread over the surface, and a bit of tin rubbed over it, which instantly unites with and covers the copper. Much care is requisite in the manipulations of this process, and independent of the tin permanently adhering to and combined with the surface of the copper, there is always a portion in excess which fuses off the first time the pan is used for frying or melting fat or butter; lead is sometimes added to the tin used in tinning, and sometimes a small quantity of mercury: it appears from Proust's detailed experiments on this subject, that the small quantity of lead thus employed can scarcely be regarded as prejudicial, and that as regards the action of acids in such cases, the tin is dissolved before the lead: the use of mercury is more objectionable.

CHARACTERS OF THE SALTS OF COPPER.—The cupreous salts are nearly all soluble in water, and of a blue or green colour. Ammonia produces a compound of a very deep blue, when added in excess to these solutions; solutions of nickel give a similar colour, but the ammoniated solutions of nickel are precipitated by potassa, which does not precipitate the corresponding cupreous combinations; hydrosulphuret of ammonia forms a black precipitate. Ferrocyanuret of potassium is also an excellent test of the presence of copper; it produces a brown cloud in solutions containing the minutest portion of the oxide; in this way the presence of less than a 20,000th part of metallic copper in solution may be detected, (provided the colour of the vehicle does not interfere,) by a reddish brown cloud, which appears in a moment or two after the application of the test*.

The metallic precipitation of copper from its solutions is effected by zinc, iron, cadmium, tin, lead, and cobalt, and, under certain circumstances,

* Mr. Alfred Taylor gives me the following caution in reference to the use of this test in organic solutions:—"In April, 1838, I examined the contents of the stomach of a person poisoned by oxalic acid: a tolerably clear liquid was obtained by boiling and filtration, and oxalic acid was easily detected. On adding solution of ferrocyanuret of potassium to a portion of the liquid, a deep claret-coloured precipitate fell down exactly like ferrocyanuret of copper. I immediately tried the liquid with polished iron and ammonia, but could find no trace of copper; the liquid was faintly acid, and after having been kept for some days, no effect was produced by the ferrocyanuret; I can only ascribe this anomalous result, to the presence of some peculiar organic compound."

feebly by bismuth. The copper sometimes appears in a clean metallic state, but is frequently alloyed by or blended with the precipitating metal, or mixed with other products. The different salts of copper are in this way differently affected. Nitrate of copper, for instance, is reduced by zinc, lead, cadmium, and tin, but when quite neutral, and out of the contact of air, iron very imperfectly and slowly acts upon it. In a common acid solution of the nitrate a plate of iron becomes immediately covered with copper. Cobalt acts very slowly, and bismuth only when heated in the solution, and then imperfectly. The reduced copper appears with its metallic lustre and peculiar colour only upon cobalt, lead, and iron; with the other metals it forms alloys of a brown or black colour. With tin, the oxide of that metal is also precipitated. Sulphate of copper is reduced by the other metals much in the same way as the nitrate: iron first becomes covered by pure copper, after which the precipitation of a subsalt of iron gives it a brown colour. The action of lead upon solution of sulphate of copper is very feeble; cobalt acts rapidly, and becomes coated with clean copper. The precipitate upon tin is accompanied by sulphate of tin, in the form of a white shining powder, but if air be excluded, protosulphate of tin remains in the solution, with a portion of sulphate of copper: in such cases the whole of the copper is never separated. Chloride of copper is easily decomposed by iron, tin, zinc, cadmium, and cobalt, and slowly by lead, provided the solution be not acid. The ammoniacal solution of oxide of copper is only reduced by zinc, iron, and cadmium, not by tin, lead, or cobalt. Zinc is by far the most effectual precipitant of copper. When the metallic precipitation of copper is resorted to for the detection of minute quantities of the metal, as for instance in cases of poisoning, iron is the preferable precipitant, and when carefully used, gives very delicate indications, and is applicable in certain cases where the other tests are interfered with by the colour of the contaminated vehicles, such as beer, wine, soup, the contents of the stomach, &c. Mr. Taylor informs me that he has in this way detected copper in gruel and the liquids just mentioned, when only 1 grain of crystallized sulphate of copper was present in 12 ounces of the liquid, and when the test by ferrocyanuret of potassium was inapplicable from the colour of the vehicle. He finds the most delicate mode of applying this test is to render the suspected liquid very slightly acid by a drop or two of dilute sulphuric acid, and then to suspend in it a clean sewing-needle; in a day or two the coating of copper becomes perceptible. When insoluble salts are thus examined, they may be moistened with dilute sulphuric acid, and rubbed upon polished iron.

The voltaic precipitation of copper is also often conveniently applicable to the detection of this metal; a few drops of the suspected liquid may be put upon clean platinum foil and touched by a wire of zinc, when a film of copper immediately coats the platinum.

Before the *blowpipe* oxide of copper is not altered by the exterior flame, but becomes suboxide in the interior. With both microcosmic salt and borax it forms a yellow-green glass while hot, but which becomes blue-green as it cools. When strongly heated in the interior flame, it loses its colour, and the metal is reduced. If the quantity of oxide be so small that the colour is not perceptible, its presence may be detected by

the addition of a little tin, which occasions a reduction of the oxide to sub-oxide, and produces an opaque red glass. If the oxide has been fused with borax, this colour is longer preserved; but if with microcosmic salt, it soon disappears by a continuance of heat. The copper may also be precipitated upon iron, but the glass must be first saturated with iron. Alkalis or lime promote this precipitation. If the glass, containing copper, be exposed to a smoky flame, the copper is superficially reduced, and the glass covered while hot with an iridescent pellicle, which is not always permanent after cooling. It is very easily reduced by soda. Salts of copper, when heated before the blowpipe, give a fine green flame.

The presence of organic substances in solutions of copper materially interferes in some cases with the action of reagents, and as, in consequence of the use of copper vessels for culinary purposes, the contamination of food by this poisonous metal is not uncommon, it often requires minute attention in judicial inquiries. (See CHRISTISON on *Poisons*, Art. COPPER; and ROSE's *Analytical Chemistry*.) In these cases precipitation by iron may, as above stated, be resorted to: or the suspected articles may be evaporated to dryness, carefully incinerated, and the residue treated by a little nitric acid: in this way a solution of nitrate of copper is obtained, to which the ordinary tests, under the precautions above pointed out, may be applied.

COPPER COINAGE.—The following table shows the standard weights, value, &c. of the copper coins of Great Britain.

COPPER COINS. Standard Weights; Remedy; Legal Tender, &c.										
Denomination of coin.	No. of pieces in the lb. avoiz.	Weight of each piece.		Value of one lb.	No. of pieces in a ton.	Value of a ton.	Remedy by Indenture.	Legal tender.	Date of proclamations fixing the amount of legal tender.	* Where current.
		In drs. avoiz.	In troy grains.							
Pence. . .	24	10·66	291·66	s. 2	53,760	£ 224	$\frac{1}{4}$ or six	12	14 Nov. 1821,	} UnitedKing- dom, and
Half-pence .	48	5·33	145·83	2	107,520	224	drms. and	6	and	
Farthings. .	96	2·66	72·91	2	215,040	224	$\frac{4}{15}$ avoiz.,	6	30 Jan. 1826.	} British Cols.
$\frac{1}{2}$ do . . .	192	1·33	36·45	2	430,080	224	or 175 tr.	
$\frac{1}{10}$ of a penny.	240	1·06	29·16	2	537,600	224	grns. per	Ionian Islands
$\frac{1}{5}$ of farthing.	288	·88	24·30	2	645,120	224	lb. avoiz-	Malta.
$\frac{1}{4}$ do . . .	384	·66	18·22	2	860,160	224	dupois.	Ceylon.
<p>The moneyers deliver the coined moneys to the Mint office in bags containing $\frac{1}{2}$ cwt. avoirdupois, in value £5 12s. 0d. The deliveries to the public are made in bags of 60 lbs. weight avoirdupois, value £5.</p>										

§ XVI. LEAD.

THE natural compounds of this metal are very numerous. The most important is the *sulphuret*, from which the pure metal is chiefly procured. Lead is also found combined with carbonic, sulphuric, phosphoric, arsenic, molybdic, and chromic acids, and with oxygen and chlorine. It seems doubtful whether lead ever occurs *native*, that is, in a pure state. To obtain lead perfectly pure, it may be dissolved in nitric acid; the solution

evaporated to dryness; the dry mass redissolved in water and crystallized; these crystals heated strongly with charcoal afford the metal.

Lead appears to have been known in the earliest ages of the world. Its colour is bluish-white; it has much brilliancy, is remarkably flexible and soft, and leaves a black streak on paper: when handled it exhales a peculiar odour. It melts at about 612° , and, by the united action of heat and air, is readily converted into an oxide which goes off in vapour: in perfectly close vessels it does not sublime at a white heat. Its specific gravity, when pure, is 11.445, but the lead of commerce seldom exceeds 11.35. Its specific heat, according to Regnault, is 0.03140. When slowly cooled it forms octoëdral crystals, and contracts considerably during its solidification, so that in bullets and castings of lead rapidly cooled there is generally a cavity. Its density is said not to be increased by hammering, yet it becomes very hot during that operation.

At common temperatures and in its ordinary state, lead undergoes little change by mere exposure to air, and is but slowly acted on by the joint agency of air and water: but when in a state of very fine division, as it is obtained diffused through charcoal, by exposing *tartrate of lead* to a red heat in close vessels, it takes fire when brought into the contact of air. In distilled water, free from air, and in close vessels, a clean surface of lead remains bright; but, under the same circumstances, in open vessels, it soon tarnishes, small crystalline scales of oxide of lead are formed, a portion of which dissolves in the water, and is again slowly precipitated in the form of carbonate: in this case the oxygen is imparted by the air held in solution in the water; the film of oxide thus formed is soluble to a small extent in the pure water, and is thrown down in proportion as it passes into the state of carbonate. A very minute trace of sulphuric acid, or of a soluble sulphate, in the water, entirely prevents this corrosive effect, and hence it is that common spring-water is kept with considerable impunity in leaden cisterns, which, however, should have *wooden* and not leaden covers; in the latter case, the vapour of the water below condenses upon the cover, and often tends to its rapid corrosion, it being in fact distilled water, and not therefore prevented in its action by any saline matters; so that when water is to be kept in this way, as it generally is for domestic use, its qualities should be cautiously inquired and examined into, as very deleterious effects have occasionally arisen from the solution of the oxide. Another source of contamination by lead may arise from electric action, as where iron or copper bars, screws, or pipes, are in contact with or soldered into lead: and in these cases, owing to the action of alkaline bases as well as of acids upon the lead, danger may occur when it is thrown into an electro-negative as well as electro-positive state. The means of detecting lead are fortunately simple and delicate, as will appear from the details we are about to give: a good epitome of all that relates to the action of water on lead, will be found in CHRISTISON'S *Treatise on Poisons* (Art. LEAD).

Exposed upon ignited charcoal to a current of oxygen gas, lead boils and burns with a blue flame, throwing off dense yellow fumes of oxide. It does not decompose water at any temperature. The alchemists gave this metal the symbol and name of *Saturn*, h_2 . The equivalent of lead is 104. (104 GMELIN, 103.6 TURNER, 103.73 GRAHAM.)

PROTOXIDE OF LEAD. ($pl + o$) or PL.—This, which is the only salifiable oxide of lead, may be formed by exposing the gray powder which gradually collects upon the surface of melted lead, to the further action of heat and air till it acquires an uniform yellow colour. It is also obtained by exposing pure nitrate, or subnitrate, or carbonate of lead, to a dull red-heat out of contact of air, and taking care to avoid fusion. When a solution of acetate of lead is dropped into a solution of ammonia, the white powder which falls is a *hydrated oxide*, which, examined by a microscope, is in the form of small prismatic crystals. Payen obtained this hydrated oxide, together with crystals of anhydrous protoxide of lead, by decomposing tribasic acetate of lead by ammonia. (*Ann. de Ch. et Ph.*, LXVI. 54.) When the protoxide is heated it has a red colour, but in its ordinary state it is lemon or orange-yellow, according to the mode in which it has been prepared, and is known under the name of *Massicot*. At a high red-heat it fuses, and forms, on cooling, a lamellar vitreous mass of a reddish-brown colour: this is often obtained in scales, under the name of *Litharge*, which, when of a red colour from the presence of minium, was called *Litharge of Gold*, the paler varieties being termed *Litharge of Silver*. When of a dark hue from the presence of a little sulphuret of antimony, these vitrified oxides are known by the German term *Abstrich*.

Protoxide of lead is a powerful salifiable base, forming neutral salts with the acids; and, in many instances, subsalts, which have an alkaline reaction; when moist or in the state of hydrate, (and even when dry, according to Berzelius,) it absorbs carbonic acid from the atmosphere, and gradually acquires the property of dissolving in acids with effervescence. It is soluble in potassa and soda, forming yellow liquids, which after a time gradually deposit micaceous or dodecaëdral crystals of anhydrous oxide of lead, probably in consequence of the slow absorption of carbonic acid by the alkali; it combines with baryta, strontia, and lime, forming compounds of sparing solubility, and easily decomposed even by the weakest acids: a paste or wash, containing hydrate of lime and oxide of lead, is used to blacken hair, which it does in consequence of the formation of a black sulphuret arising out of the combination of the sulphur in the hair with the metal of the oxide, while the lime by uniting with the oily matter facilitates the effect.

When oxide of lead is fused with the earths and metallic oxides, it forms vitreous and in some cases very fusible compounds, hence its use in the manufacture of glass; hence also the readiness with which it corrodes common crucibles when it is kept for a sufficient time in fusion in them. Heated with charcoal, this and the other oxides of lead are easily reduced to the state of metal; they are also reduced, when heated in hydrogen or coal gas. This oxide consists of

Döbereiner. Vauquelin. J. Davy. Proust. Richter.								
Lead	1	104	92·857	93·02	93	92·85	91	88·5
Oxygen	1	8	7·143	6·98	7	7·15	9	11·5
Protoxide of lead	1	112	100·000	100·00	100	100·00	100	100·0

RED LEAD. MINIMUM.—This substance, which is well known as a common red pigment, is made by exposing protoxide of lead to the action

of heat and air, so as to oxidize, without fusing it, the temperature required for this purpose being between 570° and 580° ; it gradually acquires a fine red colour, the brilliancy of which, however, goes off by exposure to light. To obtain it of a brilliant colour it requires to be made in large quantities and with several precautions. The method formerly employed in Derbyshire is described in WATSON'S *Chemical Essays*. This oxide is not salifiable, but the acids convert it into protoxide and peroxide; they combine with the former, and leave the latter in the form of an insoluble brown powder. Minium, upon the strength of the analyses of Berzelius and Vauquelin, has generally been regarded as a *sesquioxide*, but, according to Dumas, it is of variable composition. (*Ann. de Ch. et Ph.*, xlix. 398.) Phillips represents it as an oxide containing 3 atoms of lead and 4 of oxygen; and Labillardière found in a crystallized minium of a fine orange-red, which had accidentally been produced in an old red-lead furnace, 4 atoms of lead, and 5 of oxygen: the former, therefore, gives the formula $2(pl+o) + (pl+2o)$, and the latter $3(pl+o) + (pl+2o)$, while Vauquelin and Berzelius found about 10 per cent. of oxygen in the samples which they examined, and which consequently lead to the formula $(pl+1\frac{1}{2}o)$ or $(2pl+3o)$. In stating that minium may be purified by abstracting the protoxide with which it is usually mixed, by digesting it in a solution of neutral acetate of lead, Dumas obviously assumes that it is a definite compound. When exposed to a temperature somewhat above that required for its formation, minium gives off oxygen, and reverts to the state of protoxide: it was thus originally used as a source of oxygen gas by Priestley. The most perfect and brilliant minium as respects colour, is obtained by heating pure carbonate of lead in a current of air to a temperature a little short of 600° .

PEROXIDE OF LEAD. BINOXIDE OF LEAD ($pl+2o$) is obtained in the form of an insoluble brown powder by digesting minium in cold nitric acid; or by passing chlorine through minium diffused in water, or through a solution of acetate of lead, and thoroughly washing the product in hot water to remove the chloride of lead: the first is the best process, if the nitric acid used be pure; the resulting oxide only requires to be well-washed and dried at 212° .

At a red heat peroxide of lead gives off oxygen, and is converted into protoxide. Digested in liquid ammonia, a mutual decomposition takes place, and water and nitrate of lead are formed. Triturated with a fifth of its weight of sulphur, it inflames spontaneously. With hydrochloric acid, it furnishes chlorine and chloride of lead. When boiled in nitric or sulphuric acid, oxygen is evolved and salts of the protoxide are formed. It absorbs sulphurous acid gas with the evolution of much heat, or even ignition, and forms sulphate of lead; hence its use in the analysis of gaseous mixtures to separate sulphurous from carbonic acid gas. It consists of

					Berzelius.	
Lead	1	. .	104	. .	86.67	. . 86.51
Oxygen	2	. .	16	. .	13.33	. . 13.49
Peroxide of lead	1		120		100.00	100.00

DIOXIDE OF LEAD. ($2pl + o$).—When *oxalate of lead* is heated to dull redness in a small retort, carbonic oxide and carbonic acid are evolved, and a dark-gray powder remains, which is resolved by acids into protoxide and metallic lead, and which, according to Dulong, is a definite suboxide. The gray powder with which lead that has been long exposed to air, especially if heated, becomes covered, is, according to Berzelius, similar in composition. Boussingault finds that mercury triturated under water with this oxide, abstracts no lead from it, and therefore infers that it is not a mixture of metallic lead with the protoxide, notwithstanding its resolution into such a mixture by sulphuric, hydrochloric, and acetic acids (*Ann. de Ch. et Ph.*, Liv. 264), but that it consists of

Lead . . .	2	208	96.3
Oxygen . .	1	8	3.7
Dioxide of lead	1	216	100.0

Metallo-chromes.—When *thin films* of oxide of lead are formed by electrolytic action upon polished steel-plates, they give rise to those beautiful prismatic tints which Nobili originally described under the above name: the most perfect specimens which I have seen in this country were produced by Mr. Gassiot, to whom I am indebted for the following memorandum upon the subject. “Into a clear saturated solution of acetate of lead place a bright polished steel-plate, and on this a piece of thick card-board, out of which the required figure has been cut; a ring of wood of the size of the figure is then placed on the card, on which rests a copper disc, slightly concave, or convex, according as you may require the different colours: connect the positive electrode of a voltaic battery (I generally used three or four of Daniell’s cells) with the steel-plate, and the negative with the copper disc. The beauty of the figure will depend on the energy of the battery, the strength of the solution, and the time employed; but, as above, from six to fifteen seconds is sufficient. Instead of the card and copper disc, I sometimes use negative electrodes, composed of copper wire, in different forms; the colours then overlap each other with their gorgeous tints in the most beautiful manner. The ultimate size of the figure is dependent upon that of the elements used; for instance, in attempting to make a figure of about eighteen to twenty inches diameter, I found it requisite to combine two or more zincs and two or more coppers together,—the *size* of the figure depending on the *quantity*, and the *rapidity* of the production, on the *intensity* of the battery and approximation of the electrodes, that is, of the steel-plate and copper disc. (A notice of Mr. Gassiot’s experiments will be found in the *Proceedings of the Royal Society*, March, 1840.)

CHLORIDE OF LEAD. ($pl + c$).—When laminated lead is heated in chlorine, the gas is absorbed, and a *chloride of lead* results. (J. DAVY, *Phil. Trans.*, 1812.) The same substance is obtained by adding hydrochloric acid, or a solution of chloride of sodium, to nitrate of lead, washing the precipitate in cold water, and drying it at 212° ; it is also formed when the oxides of lead are digested with heat, in hydrochloric acid. It is white and fusible, and, on cooling, forms a hornlike substance (*plumbum corneum*) of the specific gravity of 5.13. It does not absorb ammonia.

(FARADAY.) It volatilizes at a high temperature provided air has access, in which case a portion of oxide of lead is also formed. It dissolves in 30 parts of water at 60° , and in 22 at 212° , separating, as its solution cools, in small anhydrous acicular crystals, unchanged by exposure to air, and of a sweetish taste. It dissolves in dilute hydrochloric and nitric acids: it is insoluble in alcohol. Chloride of lead consists of

				J. Davy.	Döbereiner.
Lead	1	104	74.3	74.22	75.758
Chlorine	1	36	25.7	25.78	24.242
Chloride of lead	1	140	100.0	100.00	100.000

Native Chloride of Lead has been found amongst the volcanic products of Vesuvius, in small acicular crystals: a *dichloride of lead* ($2pl + c$) has been found in the Mendip-hills, in Somersetshire; it forms fibrous crystalline masses upon a black ore of manganese; it is of a yellow colour; a *native oxichloride of lead* (very rare) has been found in the same locality.

OXICHLORIDE OF LEAD.—A compound of chloride and oxide of lead is sometimes prepared by acting upon a solution of common salt by litharge; solution of soda, and oxide and chloride of lead are formed; this insoluble residue, when fused, is known under the name of *patent yellow*, *Turner's yellow*, or *Cassel yellow*. When treated by nitric acid, it forms nitrate of lead, and a portion of chloride separates. A similar compound may be obtained by fusing together 1 part of chloride with 4 or 5 of oxide of lead, or by heating 1 part of sal-ammoniac with 10 of oxide of lead. According to Berzelius, a hydrated tribasic oxichloride of lead ($pl + c$) $+ 3(pl + o) + 4q$, is thrown down in the form of a white insoluble powder when ammonia is added to a solution of chloride of lead. In fusing these oxichlorides great care must be taken to avoid the presence of inflammable matter, by which they are readily discoloured in consequence of the reduction of a portion of lead; their fusion is best effected in a muffle.

CHLORATE OF LEAD ($Pl + c'$) is obtained by digesting the protoxide in chloric acid; it separates by slow evaporation, in white crystalline flakes of a very sweet taste. When heated, it gives out oxygen, and becomes a chloride. When chlorine is passed through protoxide of lead diffused in water, chloride and peroxide of lead are formed, but no chlorate. (VAUQUELIN, *Ann. de Ch.*, xciv.)

IODIDE OF LEAD ($pl + i$) may be formed by heating leaf-lead with iodine; it is most readily obtained by adding iodide of potassium to solution of nitrate of lead; it then falls in the form of a bright-yellow powder, soluble in 1250 of cold, and 200 parts of boiling water, and separates as the solution cools, in beautiful brilliant flakes. In this crystalline state it retains its colour, but the pulverulent iodide becomes pale by exposure to light. It is soluble in caustic potassa and soda, forming double salts; boiled with carbonate of potassa, it forms carbonate of lead and iodide of potassium. It consists of

				Henry.
Lead	1	104	45.22	45.1
Iodine	1	126	54.78	54.9
Iodide of lead	1	230	100.00	100.0

OXIDIDE OF LEAD.—According to Denot, there are three oxidides of lead, each containing an atom of water, which they do not lose below a temperature of 400° ; they consist respectively of $(pl+i) + (pl+o)$, of $(pl+i) + {}_2(pl+o)$, and of $(pl+i) + {}_5(pl+o)$. (GRAHAM.)

IODIDE OF LEAD AND POTASSIUM.—When excess of iodide of lead is digested in a concentrated solution of iodide of potassium, a solution is formed which yields on evaporation a mass of silky crystals; this compound is decomposed both by water and alcohol, which separate iodide of lead; it is represented by ${}_2(pl+i) + (po+i)$. When the alkaline iodide is used in excess, the resulting compound is $(pl+i) + {}_2(po+i)$. (BOULLAY.)

IODATE OF LEAD $(Pl+i')$ is thrown down in the form of a white powder on adding iodate of potassa to any of the soluble salts of lead. It redissolves in excess of the acid. (PLEISCHL.)

BROMIDE OF LEAD $(pl+b)$ is precipitated from a solution of lead by hydrobromic acid or bromide of potassium; it is fusible, and concretes on cooling into a yellow mass. When first precipitated, it is decomposed by sulphuric and nitric acids; but when fused, it requires boiling sulphuric acid to produce that effect. (BALARD, *Ann. de Ch. et Ph.*, xxxii. 359.)

BROMATE OF LEAD $(Pl+b')$ is thrown down in the form of a white powder, by adding bromic acid to a dilute solution of nitrate of lead.

FLUORIDE OF LEAD $(pl+f)$ is almost insoluble, and obtained by adding hydrofluoric acid to nitrate of lead, when it falls in the form of a white powder, soluble in nitric and hydrochloric acids, by which, when evaporated, it is decomposed. Ammonia converts the fluoride into a *sub-fluoride* of lead, which is more soluble than the former.

NITRATE OF LEAD $(Pl+n')$ is obtained by dissolving the metal, not in excess, in nitric acid, and evaporation. It crystallizes in tetraëdra and octoëdra, which have a specific gravity = 4; they are white, anhydrous, translucent, harder than alum, and of a styptic taste; they decrepitate when heated, and when distilled give out nitrous acid vapour and oxygen, and protoxide of lead remains in the retort: they are soluble in between 7 and 8 parts of water at 60° , and insoluble in alcohol. This salt is of much use in analytical chemistry as a test of the presence of free and combined sulphuric acid (except in *alkaline* solutions, which should be first neutralized with nitric acid): the precipitate (which is *sulphate of lead*) is insoluble in nitric acid. Carbonic acid, and the alkaline carbonates, phosphates, oxalates, and tartrates, form precipitates in a solution of nitrate of lead, but the precipitates are soluble in nitric acid. The iodides and bromides, and the chlorides, when not very dilute, also precipitate the nitrate of lead: all these precipitates are *white*, with the exception of those by the soluble iodides, which are *yellow*. With sulphuretted hydrogen this solution of lead forms a dark-brown or black precipitate of sulphuret of lead. Nitrate of lead is always anhydrous, and consists of

				Döbereiner.	Chevreul.
Oxide of lead . .	1	112	67.47	67.6	67
Nitric acid . .	1	54	32.53	32.4	33
Nitrate of lead	1	166	100.00	100.0	100

DINITRATE OF LEAD ($2\text{Pl} + n'$) may be formed by boiling a mixture of equal weights of nitrate and protoxide of lead in water, filtering while hot, and setting it by to crystallize; it forms pearly crystals, of a sweet astringent taste, scarcely soluble in cold water, but much more soluble in boiling water. (CHEVREUL, *Ann. de Ch.*, LXXXII.) The presence of this salt gives a yellow tint to the crystals of the neutral nitrate, which is sometimes erroneously referred to iron: it consists of

				Chevreul.	Berzelius.
Oxide of lead . .	2	224	80.58	80.14	80.5
Nitric acid . .	1	54	19.42	19.86	19.5
Dinitrate of lead	1	278	100.00	100.00	100.0

TRISNITRATE OF LEAD. ($3\text{Pl} + n' + q$).—This salt was obtained by Berzelius in the form of a white powder, by adding ammonia (not in excess) to nitrate of lead. When this salt is digested in ammonia, or when nitrate of lead is decomposed by excess of ammonia, a hydrated *sexbasic nitrate of lead* is formed ($6\text{Pl} + n' + q$).

NITRITES OF LEAD.—Chevreul and Berzelius have described three *nitrites* of lead. They are regarded by Gmelin as *hyponitrites*. They are obtained by boiling nitrate of lead with metallic lead. A detailed account of them is given by Berzelius. (*Lehrbuch*, ii.) When 78 parts of lead turnings and 100 of nitrate of lead are boiled together in water, a yellow solution, having an alkaline reaction, is obtained, which yields on cooling brilliant crystalline plates of a yellow colour, consisting of 2 atoms of oxide of lead and 1 of nitrous acid. When 100 parts of this *bibasic nitrite* of lead are dissolved in water at 166° , and mixed with 35 parts of sulphuric acid previously diluted with 4 times its weight of water, half the oxide of lead is thrown down in the form of insoluble sulphate, and a deep yellow solution remains, which on cooling deposits yellow octoëdral crystals of the *neutral nitrite of lead*. When exposed to air its solution absorbs oxygen, and when heated to 176° evolves nitric oxide, and subnitrate of lead falls. When 1 part of nitrate of lead, 1.5 of lead shavings, and 50 of water, are digested for 36 hours, at a temperature of 166° to 170° , red crystals are deposited as the liquid cools, permanent in the air, soluble in 140 parts of cold and 33 of boiling water, and having an alkaline reaction on tests; they are a *quadribasic nitrite*, consisting of 4 atoms of oxide of lead, 1 of nitrous acid, and 1 of water.

SULPHURET OF LEAD ($pl + s$) may be formed artificially by fusion: when the lead enters into fusion, it suddenly combines with the sulphur with ignition. Its lustre and colour much resemble pure lead, but it is brittle, and requires a white heat for fusion; its specific gravity is 7.58. Boiled with hydrochloric acid, chloride of lead and sulphuretted hydrogen are formed; with nitric acid it is converted into sulphate of lead. Sulphuret of lead may be obtained in the humid way, by precipitating any salt of lead by sulphuretted hydrogen; the precipitate is black, or brown if the

solution be very dilute; this is so delicate a test of lead, that, according to Pfaff, a solution containing a hundred-thousandth part of the metal is discoloured by it, provided no excess of acid be present. Sulphuret of lead consists of

				Proust.	Vauquelin.	Wenzel.	J. Davy.
Lead	1	104	86.37	86	86.23	86.8	86.9
Sulphur	1	16	13.63	14	13.77	13.2	13.1
Sulphuret of lead	1	120	100.00	100	100.00	100.0	100.0

Native Sulphuret of Lead, or *Galena*, is the principal source of the vast commercial demands of the metal. It occurs massive and crystallized, chiefly in the older secondary rocks. Its primitive form is the cube, of which there are several modifications, and among them the octoëdron. It often contains traces of silver, and sometimes in such quantity as to render it worth separating, which is effected by exposing the roasted sulphuret to the action of heat and air in shallow earthen dishes; the lead becomes oxidized and converted into litharge, while the silver is left pure, in consequence of its power of resisting the influence of heat and air. This process is called *cupellation*. The litharge is afterwards reduced by fusion with charcoal. There is a specular variety of galena, called in Derbyshire *slickensides*; and which, when touched by the miner's pick, often splits asunder with a kind of explosion.

The reduction of *galena* upon a large scale is a sufficiently simple process. The picked ore, after having been broken and washed, is roasted in a reverberatory fire, the temperature being such as to soften but not fuse it. During this operation it is raked till the fumes of sulphur are dissipated, when it is brought into perfect fusion; the lead, reduced by the fuel, sinks to the bottom, and is run out into oblong moulds called *pigs*; the scoriæ are again melted, and furnish a portion of less pure metal. The mines of Great Britain afford an annual produce of about 48,000 tons of smelted lead, of which nearly the whole is obtained from the sulphuret.

HYPOSULPHITE OF LEAD ($\text{Pb} + \text{S}$) is precipitated in the form of a white powder, by adding solution of nitrate of lead to hyposulphite of potassa. At 212° it becomes dark-coloured, and at a higher temperature it burns like tinder. Distilled in close vessels, it gives out sulphurous acid, and is converted into sulphuret and sulphate of lead. It requires more than 3000 parts of cold water for solution. It is composed of

			Herschel.
Oxide of lead	1	112	70.30
Hyposulphurous acid	1	48	29.70
Hyposulphite of lead	1	160	100.00

SULPHITE OF LEAD ($\text{Pb} + \text{S}$) may be obtained by digesting protoxide of lead in sulphurous acid; or by adding sulphurous acid or sulphite of potassa to nitrate of lead. It is white, insoluble, and tasteless. When heated it loses sulphurous acid. It is converted by nitric acid into sulphate of lead. It disengages sulphurous acid when acted upon by hydrochloric, and by sulphuric acid. It consists of

				Thomson.	Gay Lussac.
Oxide of lead	1	112	77.77	74.5	78
Sulphurous acid	1	32	22.23	25.5	22
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Sulphite of lead	1	144	100.00	100.0	100

HYPOSULPHATE OF LEAD ($\text{Pb} + \text{S}'$) is formed by digesting carbonate of lead in hyposulphuric acid, filtering and evaporating. It forms soluble crystals, which, by the action of ammonia, may be so decomposed as to yield two *subhyposulphates*: the crystals contain

				Heeren.
Oxide of lead	1	112	50.91	51.04
Hyposulphuric acid	1	72	32.73	33.01
Water	4	36	16.36	15.95
<hr/>				
Crystallized hyposulphate of lead	1	220	100.00	100.00

SULPHATE OF LEAD. ($\text{Pb} + \text{S}$).—Cold sulphuric acid has no action upon metallic lead; but when the metal is boiled in concentrated sulphuric acid, sulphurous acid is evolved, and a white sulphate of lead is formed. It is also easily produced by adding dilute sulphuric acid, or an alkaline sulphate, to a solution of nitrate of lead, when it falls in the form of a dense white powder, which the microscope shows to consist of crystalline grains; and hence the application of the soluble salts of lead, especially the nitrate and the acetate, as tests of the presence of sulphuric acid and sulphates. Dr. Thomson found, that after having been dried at a temperature of 400° , it might be heated to redness in a platinum crucible without losing weight. Heated on charcoal by the blowpipe, it is decomposed and ultimately reduced. Heated with 1 atom of carbon it furnishes, at a white heat, carbonic and sulphurous acids and protoxide of lead; with 2 atoms of charcoal it yields metallic lead. (BERTHIER.) Sulphate of lead is not *absolutely* insoluble in water: it is insoluble in alcohol and nearly so in nitric acid; concentrated hydrochloric acid decomposes it, and forms chloride of lead; but on the addition of water sulphate of lead is reproduced. It is sparingly soluble in excess of sulphuric acid, and separates from it in small prismatic crystals. It is soluble, when recently precipitated, in the fixed alkalis, and sparingly so in their carbonates. Accordingly, if a weak solution of nitrate of lead be dropped into a solution of carbonate of soda containing sulphate of soda, there is either no immediate precipitate, or, if formed, it is redissolved on stirring the liquid. Its acid is expelled by the action of silica and of alumina at a red heat, hence its decomposition when fused in earthen crucibles. Digested with an acid solution of nitrate of baryta, it yields nitrate of lead and sulphate of baryta. Sulphate of lead consists of

				Klaproth.	Berthier.	Berzelius.
Oxide of lead	1	112	73.68	73.5	73.99	73.615
Sulphuric acid	1	40	26.32	26.5	26.01	26.385
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Sulphate of lead	1	152	100.00	100.0	100.00	100.000

Native Sulphate of Lead is found in Anglesea, Scotland, and elsewhere, crystallized in prisms and in octoëdra. It is a rare mineral.

PHOSPHURET OF LEAD may be formed by dropping phosphorus into melted lead, or by calcining phosphate of lead with charcoal. It is of the

colour of lead, and soon tarnishes. When struck with a hammer it becomes luminous, and sometimes takes fire. It consists, according to Pelletier, of 88 lead + 12 phosphorus: these numbers closely correspond with

Lead	1	104	86.5
Phosphorus	1	16	13.5
Phosphuret of lead	1	120	100.0

HYPOPHOSPHITE OF LEAD has not been examined.

PHOSPHITE OF LEAD ($PL + \bar{p}$) was prepared by Berzelius by mixing chloride of lead with phosphite of ammonia. It is white, tasteless, and insoluble, and appears to consist of 1 proportional of oxide of lead + 1 proportional of phosphorous acid.

PHOSPHATE OF LEAD ($PL + p'$) is formed by mixing hot solutions of chloride of lead and phosphate of soda: according to Mitscherlich, the phosphate of soda must be dropped into the solution of lead so as to leave the latter in excess, otherwise a subphosphate of lead falls. It is white; insoluble in water and in acetic acid; soluble in fixed alkaline solutions, and in nitric acid. It is decomposed by sulphuric acid, and by hot hydrochloric acid. It fuses before the blowpipe, and the globules crystallize in small polyhedrons on cooling. It consists of

			Thomson.	Berzelius.	Berthier.
Oxide of lead	1	112	75.68	75	76
Phosphoric acid	1	36	24.32	25	24
Phosphate of lead	1	148	100.00	100	100

SESQUIBASIC PHOSPHATE OF LEAD ($\frac{11}{14} PL + p'$) is obtained by digesting the *neutral phosphate* in ammonia, or by precipitating acetate of lead by neutral phosphate of soda: it is white, less fusible than the neutral phosphate of lead, and before the blowpipe yields a mixture of metallic lead with the neutral phosphate; it consists of

			Berzelius.
Oxide of lead	$1\frac{1}{2}$	168	82.35
Phosphoric acid	$1\frac{1}{4}$	36	17.65
Sesquibasic phosphate of lead	1	204	100.00

SESQUIPHOSPHATE OF LEAD ($PL + \frac{11}{14} p'$) is the white powder which falls when a hot solution of chloride of lead is decomposed by biphosphate of soda. It reddens litmus, and consists of

			Berzelius.
Oxide of lead	1	112	67.47
Phosphoric acid	$1\frac{1}{2}$	54	32.53
Sesquiphosphate of lead	1	166	100.00

BIPHOSPHATE OF LEAD ($PL + 2p'$) is deposited in granular crystals, by solutions of the preceding phosphates in phosphoric acid.

Native Phosphate of Lead has been found in the mines of Cumberland, Durham, Yorkshire, and of Wanlock Head, in Scotland, and in many of the foreign mines. Its colour is various shades of green, yellow, and brown. Its primitive form is a rhomboid, but it usually occurs in six-sided prisms. It is semitransparent and brittle. It appears to be a

subsesquiphosphate of lead combined in variable proportions with chloride of lead. Baruel has described a *double phosphate of lead and lime* from the mine of Nussiere, near Beaujeu, in the department of Rhone: he has called it *Nussierite*. (*Ann. de Ch. et Ph.*, lxii. 219.)

NITROPHOSPHATE OF LEAD.—A crystallized combination of phosphate and nitrate of lead is obtained by evaporating a solution of phosphate of lead in nitric acid. Water decomposes it and resolves it into its component salts. (BERZELIUS.)

SELENIURET OF LEAD. (*pl + se.*)—Lead and selenium readily combine and yield a seleniuret, which has been found native in the Hartz and at Fahlun. It resembles galena, but is less brilliant. It consists of

						H. Rose.
Lead	104	72.22
Selenium	40	27.78
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Seleniuret of lead	1				144	100.00
						99.40

SELENITE OF LEAD. (*pl + se.*)—Selenious acid and the alkaline selenites occasion a white precipitate in solutions of lead, which falls in the form of a heavy powder. It is nearly as fusible as chloride of lead, and concretes on cooling into a white crystalline mass; it is almost insoluble in water, and difficultly decomposed by boiling sulphuric acid. It consists of

						Berzelius.
Oxide of lead	112	66.66
Selenious acid	56	33.34
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Selenite of lead	1				168	100.00

CARBURET OF LEAD.—The compounds described under this name are probably mixtures of finely-divided metallic lead and charcoal. They are obtained by decomposing tartrate of lead or cyanuret of lead in close vessels: the former has already been mentioned as a *pyrophorus*.

CARBONATE OF LEAD. CERUSE. WHITE LEAD. (*Pl + car.*)—This important compound of lead is made upon a large scale, and extensively employed as a white oil-paint, which is also the basis of the greater number of other colours: in England it is chiefly made in London and at Newcastle-on-Tyne, to the annual amount of about 16,000 tons. There are many processes by which it may be obtained, and much ingenuity has been displayed in their modification and improvement, the great objects being to obtain it in such a state as that it shall form the most opaque and densest *body*, as it is called, when ground up with linseed, or other drying oil, and shall at the same time be of a pure and perfect white.

The following is an outline of the several methods by which carbonate may be formed. 1. By the precipitation of any of the soluble salts of lead by means of the alkaline carbonates. A solution of nitrate or acetate of lead is thus decomposed by carbonate of soda; it yields a dense white precipitate, which, when washed and dried, is of a pure white, but when examined by a magnifier is found to consist of minute crystalline grains, a circumstance which interferes with its body or opacity to such an extent as to render it unfit for oil paint: it is also a

pure or neutral carbonate, and it will appear that the most esteemed white lead generally contains more or less oxide or hydrated oxide of lead. It varies in texture according as the carbonate is added to the nitrate, or the nitrate to the carbonate; the latter mode of precipitation, with properly diluted solutions, furnishes the most impalpable powder. When the carbonate has once acquired the crystalline texture, no grinding or mechanical comminution is capable of conferring upon it the qualities which fit it for an oil pigment. 2. When carbonic acid gas is passed through a hot solution of dinitrate of lead, carbonate of lead is thrown down, and the solution reverts to the state of neutral nitrate: this is reconverted into subnitrate by boiling with protoxide of lead (powdered litharge), and the precipitation continuously repeated. This is the basis of Messrs. Button and Dyer's patent process: they obtain carbonic acid for the decomposition of the subnitrate, by the combustion of coke, and the gas is purified from sulphurous acid and sulphuretted hydrogen by passing it through a washing apparatus, containing chalk and white lead diffused through water: the precipitated carbonate of lead is well washed, subjected to great pressure so as to condense it into cakes, and then dried in stoves. 3. Subacetate of lead (which see) is decomposed by passing through it a current of purified carbonic acid gas. The celebrated white lead of Clichy is thus prepared. 4. Granulated lead is agitated with water, by which a quantity of hydrated oxide of lead is formed, and this is subjected to the action of carbonic acid: this process was carried on in a large factory at Pimlico, under a patent granted to B. C. Torassa, Wood, and Co., but was soon abandoned. 5. Finely powdered litharge is moistened, mixed with a little acetate of lead, and submitted during constant stirring to a current of heated carbonic acid: in this process, patented by Messrs. Gossage and Benson of Birmingham, a subacetate of lead is successively formed and decomposed; a small quantity only of the original acetate therefore is required. 6. In *Hemming's* process for making white lead, nitrate of soda is distilled with the requisite quantity of sulphuric acid, by which nitric acid and sulphate of soda are formed. Oxide of lead is dissolved in the nitric acid, and the sulphate is converted into carbonate of soda, in the usual way, by heating with coal and chalk. A solution of the carbonate of soda is then added to the solution of nitrate of lead, and the results are carbonate of lead and nitrate of soda. Lastly, this nitrate of soda is treated as before described. 7. In the *Dutch process*, introduced into England about 1780, lead is cast into plates or bars, or into the form of stars, or circular gratings of six or eight inches in diameter, and from a quarter to half an inch in thickness: five or six of these are placed one above another in the upper part of a conical earthen vessel something like a garden-pot, in the bottom of which there is a little strong acetic acid. These pots are then arranged side by side, on the floor of an oblong brick chamber, and are imbedded in a mixture of new and spent tan (ground oak bark as used in the tan-yard). The first layer of pots is then covered with loose planks, and a second range of pots imbedded in tan is placed upon the former; and thus a stack is built up so as entirely to fill the chamber with alternate ranges of the pots containing the lead and acetic acid, surrounded by and imbedded in the tan. Several ranges of these stacks occupy each side of a covered building, each stack con-

taining about 12,000 of the pots, and from 50 to 60 tons of lead. Soon after the stack is built up the tan gradually heats or ferments, and begins to exhale vapour, the temperature of the inner parts of the stack rising to 140° or 150° , or even higher. The acetic acid is slowly volatilized, and its vapour passing readily through the gratings or folds of lead, gradually corrodes the surface of the metal, upon which a crust of subacetate is successively formed and converted into carbonate, there being an abundant supply of carbonic acid furnished by the slow fermentative decomposition of the tanners' bark. In the course of from 4 to 6 weeks the process is completed, and now, on unpacking the stacks, the lead is found to have undergone a remarkable change: the form of the castings is retained, but they are converted, with considerable increase of bulk, into dense masses of carbonate of lead; this conversion is sometimes entire, at others it penetrates only to a certain depth, leaving a central skeleton as it were of metallic lead, the conversion being unequal in different parts of the stack, and varying in its perfection at different seasons, temperatures, and states of the atmosphere. The stacks are so managed that they are successively being built up and unpacked. The corroded and converted gratings, or cakes, are then passed through rollers, by which the carbonate of lead (white lead) is crushed and broken up, and the central core of metallic lead (blue lead), if any remain, is easily separated: the white lead is then transferred to the mills, where it is ground up into a thin paste with water, and is ultimately reduced, by the process of elutriation or successive washings and subsidences, to the state of an impalpable powder; it is then dried in wooden bowls, placed upon shelves in a highly-heated stove, and thus brought to the state of masses easily rubbed between the fingers into a fine powder, in which the microscope does not enable us to discern the slightest traces of crystalline character. If intended for the use of the painter, it is next submitted to grinding with linseed oil; and it is found that a hundred-weight of this white lead is formed into a proper consistence with 8 pounds of oil, whereas precipitated white lead requires 16 pounds of oil for the same purpose; the one covering the surface so much more perfectly, and having so much more body than the other. It is sometimes supposed in this process that the oxygen and carbonic acid required to form the carbonate of oxide of lead are derived from the decomposition of the acetic acid; but this is evidently not the case, for not more than 100 pounds of real acetic acid exist in the whole quantity of the diluted acid contained in the several pots of each stack; and in 100 pounds of acetic acid there are not more than 47 to 48 pounds of carbon, whereas 6740 pounds would be required to furnish the carbonic acid which should convert 50 tons of lead (the average weight of that metal in each stack) into carbonate of lead. There can be no doubt then that the carbon or carbonic acid must come from the tan, and that the oxygen is partly derived from the same source, and partly from the atmosphere: the principal action of the acetic acid therefore is to form successive portions of subacetate of lead, which are successively decomposed by the carbonic acid: the action is, however, of a very remarkable description, for even masses of lead, such as blocks of an inch or more thickness, are thus gradually converted through and through into carbonate, so that if due time is allowed there is no central remnant of metallic lead. The

original texture of the lead is much concerned in the extent and rapidity of the conversion. Rolled or sheet lead will not answer, and the gratings, coils, and stars which are employed, are all of cast-lead. The purest metal is also required; for if it contain iron, the resulting white lead acquires a tawny hue, and if a trace of silver, it acquires a perceptible dinginess when it is subjected to the action of light.

In this notice of the manufacture of white lead, I have assumed that the article which occurs in commerce is a true anhydrous carbonate, and such it sometimes is; it has, however, been observed by Mulder, that it very commonly contains variable proportions of protoxide. According to his analyses, there are three varieties of commercial white-lead, represented as follows:—

No. 1.	2 atoms of carbonate of lead	+ 1 atom of hydrated protoxide of lead.
2.	5 ditto	+ 2 ditto
3.	3 ditto	+ 1 ditto

Mr. Richardson's experiments, however, as quoted by Professor Graham (*Elem. Chem.*, 591), show that the quantity of oxide in the best varieties of white lead is by no means considerable; carbonate of lead contains 16·5 of carbonic acid, and 83·5 of oxide of lead per cent. Mr. Richardson's specimens gave the following results:—

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Carbonic acid .	13·70	15·83	13·70	13·03	13·24	14·61	13·71	13·99	12·99	14·95
Protoxide of lead	86·00	83·49	85·66	85·98	86·46	84·83	86·02	86·09	86·45	85·02
	99·70	99·32	99·36	99·01	99·70	99·44	99·73	100·08	99·44	99·97

These specimens were all dried at a temperature of 300° before analysis. No. 1 was made by transmitting carbonic acid through subacetate of lead. No. 2, Krems white. Nos. 3, 4, and 5, were made by causing small pieces of lead to be agitated in a tub into which carbonic acid was passed. Nos. 6, 7, 8, 9, and 10, were made by the tan-pit process, but each by a different manufacturer.

Large quantities of sulphate of baryta are occasionally added to white lead, by which its valuable properties are proportionately deteriorated; the adulteration is easily detected by digesting the sample in dilute nitric acid, which dissolves the carbonate of lead, but leaves the sulphate of baryta; the articles known on the continent under the names of *Venice white*, *Hamburgh white*, and *Dutch white*, are avowedly mixtures of sulphate of baryta with carbonate of lead, the first of equal parts, the second 2 of the sulphate, and the third 3 of the sulphate, to 1 of the carbonate. *Clichy white*, *Krems* or *Kremnitz white*, and *Silver white*, are pure carbonate of lead. A very minute addition of indigo or of lamp-black is sometimes made to white lead to give it a slight bluish shade.

Carbonate of lead is usually in the form of a heavy white powder, insoluble in water, and very sparingly soluble in aqueous carbonic acid; its specific gravity varies from 6·4 to 6·75. It entirely dissolves with effervescence in acetic and in dilute nitric acid. It is immediately discoloured and ultimately blackened by sulphuretted hydrogen, whence the necessity of the most cautious exclusion of all sources of that compound

in white-lead works. When carefully heated in the contact of air, carbonate of lead loses carbonic acid, and furnishes by proper management a beautiful *minium*. The components of carbonate of lead are:—

				Berzelius.	Chevreul.	Klaproth.	Chenevix.
Oxide of lead . .	1	. 112	. 83.58	. 83.5	. 83.64	. 83.67	. 85
Carbonic acid . .	1	. 22	. 16.42	. 16.5	. 16.36	. 16.33	. 15
Carbonate of lead	1	134	100.00	100.0	100.00	100.00	100

Native Carbonate of Lead is one of the most beautiful of the metallic ores; it occurs crystallized, and fibrous, the former transparent, the latter generally opaque. It is soft and brittle, and occasionally tinged green with carbonate of copper, or gray by sulphuret of lead. The octoëdron is its primitive form: it also occurs prismatic and tabular. It has been found in Cumberland and Durham; and the acicular variety, of great beauty, in Cornwall.

CYANURET OF LEAD (*pl* + *cy*) falls in the form of an insoluble white powder when cyanuret of potassium is added to a solution of nitrate of lead, or when hydrocyanic acid is dropped into acetate of lead: heated to redness in a glass tube, it gives out nitrogen, and leaves the pyrophoric *carburet of lead* above noticed.

CYANATE OF LEAD (*Pl* + *cy'*) is thrown down in the form of a white crystalline precipitate when cyanate of potassa is added to acetate of lead; it is anhydrous, and consists of 77 oxide + 23 acid. (WÖHLER.)

SULPHOCYANURET OF LEAD forms yellow opaque crystals, which are obtained by mixing concentrated solutions of sulphocyanuret of potassium and acetate of lead; they are resolved by water into hydrosulphocyanic acid and a basic sulphocyanuret: this basic salt may be formed by adding sulphocyanuret of potassium to subacetate of lead; it is an insoluble crystalline powder of a yellowish white colour. (LIEBIG.)

FERROCYANURET OF LEAD. (*fe* + 2 *pl* + 3 *cy*).—When nitrate of lead is decomposed by excess of ferrocyanuret of potassium a white precipitate falls, which, when dried and gently heated, loses water. In what may be termed its *hydrated state*, it consists, according to Berzelius, of 1 equivalent of hydrocyanate of protoxide of iron, and 2 equivalents of hydrocyanate of protoxide of lead; and, after having been heated, of

				Berzelius.
Iron	1	. . . 28	. . . 8.9	. . . 8.81
Lead	2	. . . 208	. . . 66.3	. . . 65.91
Cyanogen . .	3	. . . 78	. . . 24.8	. . . 23.89
	1	314	100.0	98.61

COBALTO-CYANURET OF LEAD.—Cobalto-cyanuret of potassium causes a slight precipitate in solution of acetate of lead; on adding ammonia, the precipitation is complete; it forms a white granular powder.

BORATE OF LEAD (*Pl* + *bo*) is precipitated in the form of a white powder, when borate of soda is mixed with nitrate of lead: it fuses into a colourless glass, and probably consists of 1 atom of boracic acid and 1 atom of protoxide of lead; but it has not been analyzed. Boracic acid

and oxide of lead may be fused together in all proportions; the neutral borate so formed is extremely fusible, the baborate less so, and the triborate as hard as glass. Mr. Faraday employed this compound in conjunction with silicate of lead to form a glass for optical purposes. (*Phil. Trans.*)

ALLOYS OF LEAD.—With *potassium* lead forms a brittle and very fusible alloy; it may be obtained by fusion; and according to Serullas (*Ann. des Mines*, viii.), by exposing a mixture of 100 parts of litharge and 60 of calcined tartar to a strong heat for two hours in a covered crucible. The alloy of *sodium* is less brittle and fusible. When exposed to air, these alloys suffer decomposition in consequence of the oxidizement of the alkaline bases, and in water the lead separates unaltered and the sodium is converted into soda. (GAY LUSSAC, *Recherches Phys. Chim.*, i. 241.) The alloy of lead and *manganese* has not been examined. When lead is fused with *iron*, two alloys are obtained; that at the bottom of the crucible consisting of lead with a little iron, while the superficial portion is iron with a little lead. (MORVEAU, *Ann. de Ch.*, lvii.) With *zinc*, lead forms a hard ductile alloy. (GMELIN, *Ann. de Ch.*, ix.) With *tin*, lead forms several useful alloys which are somewhat less dense than the mean. Common *pewter* consists of about 80 parts of tin and 20 of lead. Equal parts of lead and tin constitute *plumbers' solder*. When pieces of *copper* are thrown into red-hot melted lead, they soon disappear and form an alloy of a gray colour, brittle, and granular in texture; what is termed *pot-metal* is an alloy of this kind. Lead has not been combined with *nickel*. With *cobalt* the alloys are hard and brittle, except where the lead predominates. (GMELIN, *Ann. de Ch.*, xix.)

CHARACTERS OF THE SALTS OF LEAD.—The *soluble salts of lead* have a sweet austere taste, and are characterized by the white precipitate produced by ferrocyanuret of potassium, the black by sulphuretted hydrogen, the deep-brown by hydrosulphuret of ammonia, the yellow by iodide of potassium, and the white by sulphuric acid and the soluble sulphates. The *salts insoluble in water* are dissolved by soda and potassa, or by nitric acid, when the metal is rendered manifest by sulphuretted hydrogen and other tests. When these salts are boiled with carbonate of soda, they afford carbonate of lead, which may be dissolved in acetic or dilute nitric acid, and subjected to the usual tests. Heated by the blowpipe upon charcoal, they afford a button of metal. Lead is precipitated from its solutions, in the metallic state, by many of the other metals. Zinc and cadmium separate metallic lead from the nitrate: iron only effects its partial decomposition when in a very dilute state. Chloride of lead is slowly but entirely reduced by zinc, cadmium, and iron, but tin produces no effect except free hydrochloric acid be present. All the difficultly-soluble salts of lead may be decomposed and reduced, by mixing them with dilute hydrochloric acid, and immersing a plate of zinc in the liquid. Zinc, cadmium, and tin, decompose the *alkaline* solutions of oxide of lead, but iron is without action upon them. The appearance of the metallic lead, in these cases, depends upon the state of the solution, which, if concentrated, yields it in dull dendritic crystals, but if dilute, in large metallic leaves.

§ XVII. ANTIMONY.

THIS metal was first made known by Basil Valentine, towards the end of the 15th century. It is found *native* in Sweden, in France, and in the Hartz; but its principal ore is the *sulphuret*, the *stibium* of the ancients, which is found massive and crystallized, and of which there are several varieties. The most common is the *radiated*, which is of a gray colour, brittle, and frequently crystallized in four and six-sided prisms.

Antimony is obtained from the native sulphuret by the following process: Mix 4 parts of the powdered ore with 3 of tartar and $1\frac{1}{2}$ of nitre, and throw the mixture by spoonfuls into a red-hot crucible; then heat the mass to redness, and a button will be found at the bottom of the crucible, which is the metal as it commonly occurs in commerce, and is nearly pure. The scoriæ upon the surface contain sulphuret of potassium and antimony. Antimony may also be procured by carefully roasting the native sulphuret so as to convert it into oxide of antimony, which oxide is then reduced to the metallic state by fusion with black flux, or with the addition of common soap; a button of antimony is thus obtained, which, however, contains traces of iron and generally of potassium, and perhaps some other metals; it is further purified by again fusing it with about one-fourth its weight of oxide of antimony; on cooling, the impurities are found in the superficial slag, and the metal underneath is extremely pure.

Antimony is of a silvery-white colour, brittle and crystalline in its ordinary texture, so that when broken it exhibits splendid facets, and the surface of the ingot as it has cooled in the crucible generally has a beautiful stellated appearance; the alchemists considered this star as a mysterious guide to the secrets of transmutation. It fuses at about 800° , or at a dull red-heat, and is volatile at a white heat. Its specific heat, as determined by Regnault, is 0.05077. Its specific gravity is 6.712. (HATCHETT, *Phil. Trans.*, 1803.) Placed upon ignited charcoal, under a current of oxygen gas, antimony burns with great brilliancy, throwing off its oxide in the form of a dense yellow smoke. The equivalent of antimony is 65. (64.5 GMELIN, 64.62 TURNER.) Its symbol is *an* or *Sb* (stibium).

ANTIMONY AND OXYGEN.—Some difference of opinion has prevailed among chemists respecting the number of the definite oxides of antimony: it is probable that there are at least three, of which one only, the protoxide, is salifiable. The composition of these oxides has also been variously stated, and difficulties have occurred in assimilating them to the atomic theory: the most accurate and satisfactory experiments upon the subject are those of Berzelius (*Ann. de Ch. et Ph.*, xvii.), from which it would appear that the oxygen in the protoxide is to that in the peroxide, not as 1 to 2 but as 1.5 to 2.5, or as 3 to 5, and that in the three oxides, 1 atom of antimony is united with 1.5, 2, and 2.5 of oxygen; it will be found that in the constitution of the oxides there are analogies between antimony and arsenic.

PROTOXIDE OF ANTIMONY. SESQUIOXIDE OF ANTIMONY. ($an + \frac{1}{2}O$) or AN , or ${}^2Sb + 3O$. Graham doubles the equivalent of antimony, and

therefore represents this oxide by $(an+3o)$ or SbO_3 .—It is thus obtained: (1.) To 200 parts of sulphuric acid add 50 parts of powdered metallic antimony, boil the mixture to dryness, and wash the dry mass, first in water, and then with a weak solution of carbonate of potassa; a white powder remains, which, when thoroughly washed with hot water, is *protoxide of antimony*. (2.) It may also be procured by digesting finely-powdered sulphuret of antimony in about four times its weight of hydrochloric acid, sulphuretted hydrogen is evolved, and a solution of chloride of antimony is formed which may be decomposed by excess of carbonate of potassa, carbonic acid escapes, and protoxide of antimony falls, which is collected on a filter, washed, and dried at 212° ; it is then anhydrous. (3.) When ammonia is added to a concentrated solution of tartrate of potassa and antimony, and heat applied to the mixture, a white powder falls, which, when washed and dried, is protoxide of antimony. (4.) Dumas gives the following as an economical method of preparing this protoxide: Heat pulverized antimony in a shallow vessel exposed to air, so as to oxidize it; when the oxidation has advanced, it takes fire and becomes ignited throughout, and the protoxide passes into antimonious acid, but is mixed with metallic antimony; the whole is then transferred to a crucible in which it is heated till it fuses, when the antimonious acid is reduced to the state of protoxide by the excess of the metal, and a mass of fused protoxide and a button of metallic antimony are the results.

Protoxide of antimony is white, fusible, and volatile at a red heat, undergoing no change in close vessels, but condensing in acicular crystals; after fusion it concretes into a silky crystalline mass of a gray colour; if air be present, it undergoes a kind of combustion, and passes into the state of deutoxide. It is decomposed by sulphur and charcoal, and when acted on by nitric acid, is converted into peroxide; if heated with chlorate of potassa, it deflagrates and also becomes peroxidized; it is soluble in hydrochloric acid, and it forms emetic tartar when boiled in solution of bitartrate of potassa. When recently precipitated, and digested in caustic potassa, it is partly converted into a gray powder, which is a compound of the oxide and the alkali, very difficultly soluble. A similar combination may be obtained with soda and ammonia. When metallic antimony in fusion is exposed to a bright red-heat with the imperfect access of air, it is converted into an oxide, which appears to be the protoxide, and which condenses in long and delicate needles when sublimed; this was formerly called *Argentine flowers of Antimony*. This is the only salifiable oxide of antimony: it consists of

				Proust.	Berzelius.	J. Davy.
Antimony	1	65	84.4	81.5	84.319	85
Oxygen	$1\frac{1}{2}$	12	15.6	18.5	15.681	15
Protoxide of antimony	1	77	100.0	100.0	100.000	100

DEUTOXIDE OF ANTIMONY. ANTIMONIOUS ACID, $(an+2o)$ or $2Sb4O$, or according to Graham SbO_4 , is the result of the above-mentioned combustion of the protoxide. It is also obtained by exposing the peroxide to a red heat. It is white, but assumes a yellow colour when heated; fixed and infusible in the fire; nearly insoluble in nitric acid and sulphuric acid, and sparingly soluble in hydrochloric acid, from which it is precipitated

on dilution; when this hydrochloric solution is carefully evaporated, the deutoxide is sometimes obtained in nacreous acicular crystals. It readily combines with potassa by fusion, and the resulting compound (*antimonite of potassa*) dissolves in water, and furnishes, upon the addition of an acid, a white precipitate of *hydrated deutoxide*, which, when thoroughly edulcorated, has the property of reddening litmus. It consists of

	Proust. Thenard. Berzelius. Thomson.							
Antimony	1	65	80.25	77	80	80.127	80.84	
Oxygen	2	16	19.75	23	20	19.873	19.16	
Deutoxide of antimony } or antimonious acid }	1	81	100.00	100	100	100.000	100.00	

SALTS OF THE ANTIMONIOUS ACID. ANTIMONITES.—These compounds have been examined by Berzelius. (NICHOLSON'S *Journal*, xxxv.) They are formed by double decomposition with the solution of antimonite of potassa. In these salts the oxygen in the base is to that in the acid as 1 to 4.

ANTIMONITE OF POTASSA is formed by fusing a mixture of potassa and antimonious acid; the product is washed in cold water to remove excess of alkali; the residue is resolved by boiling water into a soluble antimonite consisting of 23 potassa + 77 antimonious acid, and into an insoluble antimonite in which there is excess of the acid.

ANTIMONITE OF LIME is a white crystalline powder, of difficult solubility in water.

ANTIMONITE OF BARYTA.—Antimonite of potassa added drop by drop to a boiling solution of chloride of barium causes a gradual deposit of silky acicular crystals, sparingly soluble in water, and permanent in the air.

ANTIMONITE OF MANGANESE is white and moderately soluble in water.

ANTIMONITE OF COBALT is a bulky lilac-coloured precipitate having no appearance of crystallization; it dissolves in hot water; when dried in the air, it retains 25 per cent. of water.

ANTIMONITE OF COPPER is a bulky green insoluble powder.

ANTIMONITE OF LEAD is an insoluble white powder.

PEROXIDE OF ANTIMONY. ANTIMONIC ACID, ($an + 21o$), or $AN', 2Sb + 5O$ TURNER, (SbO_5 GRAHAM,) is procured: 1. By acting for a considerable time upon the powdered metal, by excess of hot nitric acid, and exposing the product to a heat of about 500° . 2. By dissolving antimony in nitrohydrochloric acid, evaporating to drive off the excess of acid, and then pouring water upon the residue: the antimonious acid separates (in the form of hydrate); when washed upon a filter and carefully dried at about 500° it becomes anhydrous: at a red heat it gradually loses such proportion of its oxygen as to become antimonious acid (or deutoxide). 3. When antimoniate of potassa is decomposed by nitric acid, nitrate of potassa and hydrated antimonious acid ($an + 21o$) + ($h + o$) are the results. The *diaphoretic antimony* and *Bezoar mineral* of old *Pharmacopœiæ* consisted of this oxide, which, compared with the protoxide, is nearly

inert. Antimonic acid is pale yellow, tasteless, and insoluble in water. It neither fuses nor volatilizes at a bright red-heat, but loses oxygen and becomes antimonious acid: when exposed to the flame of a spirit-lamp urged by a blowpipe, it passes off slowly in white fumes. It does not decompose the alkaline carbonates in the humid way, but at a red heat it expels their carbonic acid, and combines with the base. It dissolves in the liquid caustic alkalis, and in hydrochloric acid when in the state of hydrate; but after exposure to a dull red-heat, becomes of extremely difficult solubility. It consists of

				Thenard.	Thomson.	Berzelius.	Proust.
Antimony	1	65	76.5	68	73.33	76.34	77
Oxygen	2½	20	23.5	32	26.67	23.66	23
Peroxide of antimony } or antimonious acid }	1	85	100.0	100	100.00	100.00	100

SALTS OF THE ANTIMONIC ACID. ANTIMONIATES. — These salts are obtained chiefly by double decomposition; as by adding the antimoniate of potassa to the soluble salts of the other metals: they are mostly difficultly soluble or insoluble. In the neutral antimoniates the oxygen in the base is to that in the acid as 1 to 5. (BERZELIUS, *Nicholson's Journal*, xxxv.)

ANTIMONIATE OF AMMONIA is formed by digesting antimonic acid in ammonia. On evaporation a *super-antimoniate of ammonia* is obtained in the form of a white powder.

ANTIMONIATE OF POTASSA is contained in the white powder obtained by igniting a mixture of 6 parts of nitre and 1 of antimony, and washing the residue with cold water. It partially dissolves in hot water, and this solution produces precipitates of insoluble antimoniates in several other metallic solutions: an antimoniate with excess of acid remains undissolved.

ANTIMONIATE OF LIME.—Solution of antimoniate of potassa dropped into chloride of calcium produces a precipitate, at first redissolved, but afterwards permanent and adhering to the glass like carbonate of lime.

ANTIMONIATE OF BARYTA is a light flocculent insoluble powder, from which dilute nitric acid abstracts the baryta and leaves the acid: it is formed by adding antimoniate of potassa to chloride of barium.

ANTIMONIATE OF MANGANESE is a white powder, permanent in the air and little soluble in water. When heated it gives out water and becomes gray: at a red heat it again becomes white.

ANTIMONIATE OF IRON. — Antimoniate of potassa throws down a white precipitate in the protosalts of iron, which becomes yellowish when removed from the solution and dried. When heated it gives out water and reddens. Before the blowpipe it is reduced; the antimony is volatilized, and iron obedient to the magnet remains.

ANTIMONIATE OF ZINC, precipitated by antimoniate of potassa from sulphate of zinc, is a white crystalline powder, very sparingly soluble in water: it gives out water and becomes yellow when heated: it is not reduced by the blowpipe on charcoal.

ANTIMONIATE OF COBALT is a red crystalline precipitate, sparingly soluble in water.

ANTIMONIATE OF NICKEL is an insoluble greenish-white powder.

ANTIMONIATE OF COPPER is a bulky green insoluble precipitate. Before the blowpipe it leaves a button of copper and antimony.

ANTIMONIATE OF LEAD is an insoluble white powder, becoming yellow when heated, and reducible before the blowpipe into an alloy of lead and antimony.

ANTIMONY AND CHLORINE. PROTOCHLORIDE OF ANTIMONY. SESQUICHLORIDE OF ANTIMONY. ($an + 1\frac{1}{2}C$.)—The powdered metal takes fire when thrown into gaseous chlorine, and a compound, at first liquid, but afterwards concreting (if the antimony be in excess), is formed. This compound may be more definitely produced by the distillation of 1 part of powdered metallic antimony with $2\frac{1}{2}$ of perchloride of mercury; or by dissolving the protoxide of antimony in hydrochloric acid, and evaporating to dryness out of the contact of air.

The protochloride of antimony is a soft solid at common temperatures, but becomes liquid by a gentle heat, and crystallizes as it cools. It is the *butter of antimony* of old writers. It deliquesces by exposure to air, and is a powerful caustic. When water is added to this chloride of antimony, a mutual decomposition ensues, and hydrated oxichloride of antimony and hydrochloric acid result. It slowly absorbs about 6 per cent. of ammonia: the compound does not deliquesce, but the ammonia is entirely expelled by a gentle heat. Protochloride of antimony consists of

				H. Rose.	Gobel.	J. Davy.
Antimony	1	65	54.6	53.27	54.98	60.42
Chlorine	$1\frac{1}{2}$	54	45.4	46.73	45.02	39.58
Protochloride of antimony	1	119	100.0	100.00	100.00	100.00

Protochloride of antimony is sometimes used for bronzing metals, especially gun barrels, which are cleaned and rubbed over with it: a film of antimony is precipitated upon the iron: some sulphate of copper is generally added to the chloride of antimony.

PERCHLORIDE OF ANTIMONY ($an + 2\frac{1}{2}C$) is formed by passing dry chlorine over heated antimony. It is a volatile transparent liquid, which emits copious fumes when exposed to air. When dropped into water a hydrated peroxide of antimony falls, and hydrochloric acid is formed. (ROSE, *Ann. of Phil.*, N. S., x.) It consists of

				H. Rose.
Antimony	1	65	41.9	40.56
Chlorine	$2\frac{1}{2}$	90	58.1	59.44
Perchloride of antimony	1	155	100.0	100.00

OXICHLORIDE OF ANTIMONY. — When protochloride of antimony is mixed with a large quantity of water, a precipitate falls, which was formerly used as an emetic, under the name of *Algarotti's powder*, or *Mercurius vitæ*. The same compound is formed on diluting a solution of antimony in nitrohydrochloric acid. When first thrown down it is white and curdy, but afterwards assumes a yellowish-gray colour and

becomes pulverulent or crystalline: it does not dissolve in water: it is fusible, and concretes on cooling into a translucent crystalline mass. By continued washing with hot water, and by the action of the alkaline carbonates, it leaves sésquioxide. According to Phillips, Johnston, and Malaguti, this compound consists of 2 atoms of the sesquichloride + 9 of the sesquioxide.

CHLORATE OF ANTIMONY has not been examined.

SESQUIODIDE OF ANTIMONY.—Antimony and iodine combine when triturated together, and form a brown compound, fusible and volatile without decomposition; acted upon by water, it produces hydriodic acid and an oxiodide of antimony. When powdered antimony and iodine are boiled together in water, hydriodic acid and protoxide of antimony are the results.

IODATE OF ANTIMONY is unknown.

SESQUIBROMIDE OF ANTIMONY.—The action of bromine on antimony is attended by the disengagement of heat and light, and the compound is readily obtained by distillation, as in the process for preparing bromide of arsenic: it is solid at common temperatures, is fused at 206° , and boils at 518° . It is colourless, and crystallizes in needles; it attracts moisture from the air, and is decomposed by water. (SERULLAS.)

SESQUIFLUORIDE OF ANTIMONY is a white solid compound, more volatile than sulphuric acid. (DUMAS, *Ann. de Ch. et Ph.*, xxxi. 435.)

NITRIC ACID acts powerfully on metallic antimony, and, if mixed with it in fine powder, will sometimes cause its inflammation: the metal becomes peroxide, and scarcely an appreciable portion is retained in solution. As in some other cases of the vehement decomposition of nitric acid, ammonia is produced, which may be rendered sensible by pouring potassa on the white magma that results, and by which the nitrate of ammonia is decomposed. Protoxide of antimony, digested in dilute nitric acid, produces a difficultly-soluble salt, which separates in white scaly crystals, and which appears to be a *nitrate of antimony*.

NITROHYDROCHLORIC ACID readily dissolves antimony, and forms an orange-coloured solution, which is decomposed by the addition of water. Iron or zinc immersed into this solution throw down a black powder, which, according to Thenard, is pyrophoric.

SULPHURET OF ANTIMONY. SESQUISULPHURET OF ANTIMONY. ($an + \frac{1}{2}s$) $2Sb + 3S$ TURNER, $Sb S_3$ GRAHAM.—This compound may be formed artificially by fusing the metal with sulphur. Its colour is dark-gray and metallic; its specific gravity 4.36. It closely resembles the *native sulphuret*. When this sulphuret is exposed under a muffle to a dull red-heat, it gradually loses sulphur, and absorbs oxygen, being converted into a gray powder, which consists of a mixture of protoxide of antimony and sulphuret. If the heat be increased, this fuses into a transparent substance of a yellow or brown colour, formerly called *Glass of antimony*, the composition of which is variable; it generally contains about 85 per cent. of protoxide and 15 of sulphuret. In that which is imported for pharma-

ceutical purposes, from Germany and Holland, there is usually a portion of silicious earth, and it is sometimes adulterated with oxide of lead. This fraud is detected by digesting the finely-powdered glass in hot nitric acid, diluting the solution, and filtering. The filtered liquor gives a white precipitate on the addition of sulphate of soda, if lead be present. During the formation of glass of antimony, if the heat be raised too high, the greater part of the oxide sublimes in slender crystalline needles, (which are generally regarded as protoxide, but which Mr. Phillips found perfectly insoluble in a solution of bitartrate of potassa;) while another portion, if air be not excluded, passes into the state of deutoxide, and undergoes no further change at a very high temperature. Compounds of the protoxide with larger quantities of the sulphuret have been termed *Saffron of antimony* or *Crocus metallorum*, and *Liver of antimony*.

When sulphuret of antimony is deflagrated with nitre, the residue consists of sulphate and antimoniate of potassa. When boiled with sulphuric acid, sulphur is separated, sulphurous acid evolved, and a sulphate of antimony is formed, from which water precipitates a subsulphate. With hydrochloric acid, sulphuretted hydrogen is evolved, and a solution of chloride of antimony in hydrochloric acid is formed, together with more or less of the sulphuretted oxide. Chlorine passed over heated sulphuret of antimony forms chloride of sulphur and sesquichloride of antimony. With nitrohydrochloric acid it yields chloride of antimony and sulphur, and if there be excess of nitric acid, sulphate and peroxide of antimony are also produced. Hydrogen gas passed over this sulphuret at a red heat, carries off the sulphur in the form of sulphuretted hydrogen, and metallic antimony remains. Charcoal decomposes sulphuret of antimony at high temperatures, and sulphuret of carbon and metallic antimony are the results: it is also desulphurized by the action of iron and some other metals, at high temperatures. This sulphuret of antimony, whether native or artificial, consists of

	Berzelius. Bergman. J. Davy. Vauquelin.						
Antimony	1	65	73	72.8	74	74.16	75
Sulphur	1½	24	27	27.2	26	25.84	25
Sesquisulphuret of antimony	1	89	100	100.0	100	100.00	100

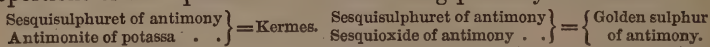
KERMES MINERAL. GOLDEN SULPHURET OF ANTIMONY.— Under these names, and also under those of *Precipitated sulphuret of antimony* and *Oxisulphuret of antimony*, certain products have been described of variable composition, and respecting the nature of which chemists are not agreed.

When solutions of antimony are decomposed by sulphuretted hydrogen, red, brown, or orange-coloured precipitates result, which vary in appearance and composition with the nature of the solution. The most definite combination of this kind is that which is thrown down when sulphuretted hydrogen is passed through an aqueous solution of the tartrate of antimony and potassa (emetic tartar). It is of a red colour inclining to orange, and when dried in the air retains its colour: it was generally considered as a compound of sulphuretted hydrogen and sesquioxide of antimony (hydrosulphate of antimony); and, inasmuch as when heated it loses water and passes into the state of gray sulphuret of antimony, it

was presumed that, under such circumstances, there was a mutual decomposition of the oxide and the sulphuretted hydrogen. But it has been found that this precipitate may be rendered anhydrous by careful drying, and that it still retains its red colour; but that when more strongly heated it shrinks in bulk and suddenly assumes the colour and lustre of the gray sulphuret: hence it has been regarded as a hydrated sesquisulphuret of antimony, and its colour (and medicinal activity?) have been referred to its state of division.

Kermes mineral is generally prepared as follows:—Equal parts of sulphuret of antimony and of potassa are fused together; the resulting mass is finely powdered, and boiled in ten times its weight of water. The liquor is filtered while hot; and, during cooling, it deposits *kermes*. The mother-liquor of *kermes* deposits a copious yellowish-red precipitate upon the addition of dilute sulphuric acid, which, when washed and dried, is known under the name of *Golden sulphur of antimony*.

According to Berzelius, when 3 atoms of potassa and 1 of sesquisulphuret of antimony are fused together, they yield 3 atoms of sulphuret of potassium and 1 of sesquioxide of antimony. The sulphuret of potassium unites with undecomposed sesquisulphuret of antimony, forming a double sulphuret or sulphur salt; and the sesquioxide of antimony unites to undecomposed potassa, to form antimonite of potassa; so that when hot water is added, a solution is obtained, holding the double sulphuret of antimony and potassium, and antimonite of potassa. As the solution cools sesquisulphuret of antimony subsides, merely because the solvent power of the sulphuret of potassium is diminished by cooling, and it carries down with it a variable quantity of antimonite of potassa, apparently in combination, inasmuch as it cannot be removed by washing. The cold solution still contains double sulphuret of antimony and potassium, and also antimonite of potassa: on adding to it the dilute acid the sulphuret of potassium becomes converted into sulphuretted hydrogen and potassa (by decomposition of water), and the antimonite of potassa is decomposed by the abstraction of its potassa; so that the sesquisulphuret and the sesquioxide of antimony being both deprived of the principles which gave them solubility, are precipitated in the form of what is called *golden sulphuret*, and which differs from *kermes* in the absence of potassa and in containing more oxide of antimony, and perhaps, as Dr. Turner observes, in being, or containing, an oxisulphuret. The following, therefore, are the components of *kermes* and the golden sulphuret, the relative proportions of their proximate elements being probably indefinite:—



The *oxisulphuret of antimony* of the Pharmacopœia is probably a mixture of *kermes* and of the golden sulphuret; it is necessarily somewhat indefinite in its composition, and therefore objectionable as a medicine: the medical powers of the sulphuret precipitated by sulphuretted hydrogen from a solution of emetic tartar have not been well ascertained, but it would be an advantage if some definite oxisulphuret of antimony could be substituted for the above: it is certainly not very probable that a highly active antimonial, medicinally, should be a mere sulphuret of antimony, owing its activity to its state of mechanical division; whether

kermes is a mixture or a combination of sesquisulphuret of antimony with antimonite of potassa has not been determined, but it is probable that either oxide of antimony or antimonite of potassa are essential to its medicinal powers, and therefore, any mere sulphuret of antimony ought not to bear the name of kermes. Mr. Phillips gives the following as the composition of the "*Antimonii oxysulphuretum*" of the Pharmacopœia. (*Transl. Lond. Pharm.*)

Sesquioxide of antimony .	12.0
Sesquisulphuret of antimony	76.5
Water	11.5
	<hr/> 100.0

The question respecting the nature of the above-mentioned golden sulphuret, is simplified by considering it merely in reference to the precipitation of solution of protoxide of antimony by sulphuretted hydrogen. When a solution of emetic tartar (which contains the protoxide of antimony), acidulated by tartaric acid, is decomposed by sulphuretted hydrogen, the precipitate which falls, when collected, edulcorated by hot water, and dried at 212° , is hydrosulphuretted protoxide of antimony $(an + 14o) + 14(s + h)$. When heated, water is evolved and sesquisulphuret of antimony remains; or we obtain $14(h + o)$ and $(an + 14s)$. When it is obtained by the other more complicated processes it varies in composition and in medicinal activity, containing probably a compound of oxide of antimony and potassa, and a portion of the double sulphuret of potassium and antimony, which is one of Berzelius' *sulphur salts*.

OXISULPHURET OF ANTIMONY.—It has already been stated that *glass of antimony* is a compound of sulphuret and oxide of antimony, and that some of the other medicinal preparations of antimony, just described, are analogous combinations of variable proportions of the sulphuret and oxide. To this class of compounds belongs also the beautiful and rare *ore of antimony*, called *red antimony*; it generally occurs in delicate capillary crystals, consisting, according to H. Rose, of 2 atoms of sesquisulphuret and 1 of sesquioxide of antimony.

SULPHITE OF ANTIMONY is an insoluble white salt, obtained by digesting the protoxide in sulphurous acid, or by passing sulphurous acid into protochloride of antimony.

SULPHATE OF ANTIMONY is the white saline mass formed by boiling powdered antimony in sulphuric acid. Water resolves it into an insoluble *subsulphate* and a soluble *supersulphate*: the latter may be obtained in small deliquescent acicular crystals by evaporation.

IODOSULPHURET OF ANTIMONY is procured, according to Henry and Garot by triturating together equal parts of iodine and sulphuret of antimony; it is of a reddish-brown colour, and when heated gives a red vapour, which condenses in red laminæ. It consists of 23.2 antimony, 67.9 iodine, 8.9 sulphur. This compound is very fusible and volatile, and is decomposed at a high temperature. Acted on by water it yields protoxide of antimony, sulphur, and hydriodic acid: its taste is acrid and disagreable.

SELENIURET OF ANTIMONY.—Selenium and antimony readily combine with evolution of heat; the compound has metallic lustre and crystalline fracture.

PHOSPHURET OF ANTIMONY is formed by heating together equal parts of oxide of antimony, phosphoric acid, and charcoal. It is white and brittle. (PELLETIER.)

Nothing is known respecting either the *Hypophosphite* or the *Phosphite* of antimony.

PHOSPHATE OF ANTIMONY.—When protoxide of antimony is digested in phosphoric acid it is dissolved, but affords no crystallizable salt on evaporation.

ANTIMONIAL POWDER.—In the *London Pharmacopœia* there is a preparation called *Pulvis Antimonialis Compositus*, formed by heating 1 part of sulphuret of antimony with 2 of hartshorn-shavings. The action of heat upon the sulphuret has already been described. Its effect upon the hartshorn-shavings is to destroy the animal matter, leaving little else than phosphate of lime. So that the *Pulvis Antimonialis* consists essentially of an oxide of antimony, mixed with phosphate of lime. This preparation is usually considered analogous to, if not identical with, *James's Powder*, which, according to Dr. Pearson's analysis (*Phil. Trans.*, 1791), consists of 43 phosphate of lime, and 57 oxide of antimony. Be this as it may, the antimonial powder of the *Pharmacopœia* is an uncertain and ill-contrived preparation: its activity depends upon the proportion of protoxide which it contains; but a great part of the protoxide may be volatilized, or converted into deutoxide, of a mixture of which, with phosphate of lime, the antimonial powder generally consists. Accordingly, in examining antimonial powder from various sources, prepared after the direction of the *Pharmacopœia*, it is found of variable composition; and it is very difficult so to conduct the process as to obtain, upon the large scale, an uniform product. For medical use, *emetic tartar* seems the only certain and necessary preparation of antimony; if, however, a compound of the nature of the antimonial powder be requisite, one of the best modes of preparing it would be to dissolve certain proportions of protoxide of antimony and phosphate of lime in hydrochloric acid, precipitate by ammonia, and edulcorate with water. Mr. Chenevix advises for this purpose equal parts of the oxide and phosphate, but such proportion of antimony is too great. (See in reference to the composition and properties of James's powder and antimonial powder, PEREIRA, *Mat. Med.*, 404.)

Neither *Carbonate*, *Cyanuret*, nor *Borate* of antimony are known to exist.

ALLOYS OF ANTIMONY.—With *potassium* and *sodium* antimony forms white brittle compounds, destructible by the action of air and water. The alloy of *potassium* and *antimony* may be formed by heating to redness in a covered crucible a mixture of equal parts of finely-powdered antimony and tartar for about three hours. When cold, the crucible must be broken, the button of alloy freed from the scoriæ, broken into pieces, and preserved in a well-stopped phial. By substituting tartrate of soda for common tartar the alloy of *sodium* and *antimony* may be obtained:

and a mixture of soda-tartrate of potassa and powdered antimony, yields the *triple alloy of antimony, potassium, and sodium*. When these alloys are reduced to powder, and exposed to air, they heat, and take fire like pyrophorus, and if blended with excess of carbon they burst into sudden ignition on exposure, and especially on the addition of a few drops of water. (SERULLAS, *Ann. des Mines*, vi.) Nothing is known of the alloys of antimony with the other light metals, nor with *manganese, cadmium, or cobalt*. Antimony and iron combine by fusion, and form a white alloy, the density of which exceeds the mean of its components. 2 parts of sulphuret of antimony fused with 1 of iron, yield a slag of sulphuret of iron, and an alloy which was formerly called *Martial regulus*. The magnetic quality of iron is more diminished by antimony than by any other metal. (GELLERT.) Zinc and antimony form a hard brittle alloy of the colour of steel, the density of which is below the mean. (GELLERT.) It is very combustible. Antimony and tin may be fused together in various proportions: an alloy of 1 atom of each is brittle and pulverizable: its specific gravity is 6.803. (CHAUDET.) 1 part of antimony and 10 of tin form a ductile compound, which a little lead renders brittle. A fine pewter is said to consist of 12 parts of tin and 1 of antimony, with a small addition of copper. When 1 part of nickel and 2 of antimony are fused together they form a dark-gray compound. (GEHLEN.) Copper combines with antimony by fusion, and when the alloy contains equal weights of the two metals, it is of a violet colour. (GELLERT.) An alloy of 1 of antimony and 3 of copper is lamellar and brittle, but takes a good polish. When there is excess of antimony the alloy is white. Lead and antimony form an important alloy: when the metals are in equal weights, the compound is brittle: 3 of lead and 1 of antimony form a compact hard alloy: 12 of lead and 1 of antimony give a very malleable alloy, harder than lead. *Type metal* is a compound of 4 parts of lead and 1 of antimony; its hardness is such as to resist the pressure to which in the printing press the type is necessarily subjected; it is readily fusible and takes a very sharp impression from the matrix or mould in which the letter or stereotype plate is cast. A good *white metal*, used for spoons and tea-pots, and sometimes called *Britannia metal*, is composed of 100 tin, 8 antimony, 2 bismuth, and 2 copper*.

* As a specimen of the *analysis* of antimonial compounds, I subjoin Mr. Hatchett's instructive examination of the *native triple sulphuret of lead, antimony, and copper, or Bournonite*.

A. 200 grains of the ore, reduced to a fine powder, were put into a glass matrass, and two ounces of hydrochloric acid being added, the vessel was placed in a sand-bath. As this acid, even when heated, scarcely produced any effect, some nitric acid was gradually added, by drops, until a moderate effervescence began to appear. The whole was then digested in a gentle heat, during one hour, and a green-coloured solution was formed, whilst a quantity of sulphur

floated on the surface, which was collected, and was again digested in another vessel, with half an ounce of hydrochloric acid. The sulphur then appeared to be pure, and, being well washed and dried on bibulous paper, weighed 34 grains; it was afterwards burned in a porcelain cup, without leaving any other residuum than a slight dark stain.

B. The green solution, by cooling, had deposited a white saline sediment; but this disappeared upon the application of heat, and the addition of the hydrochloric acid in which the sulphur had been digested. The solution was perfectly transparent, and of a yellowish-green; it was made to boil, and in this state

CHARACTERS OF THE SALTS OF ANTIMONY.—When chloride of antimony is dropped into water, and the precipitate redissolved by hydrochloric acid, the solution is acted upon by reagents as follows:—Solutions of potassa, and of ammonia, and their carbonates, produce white precipitates, insoluble in excess of potassa. Oxalic acid, phosphate of soda, and ferrocyanuret of potassium produce white precipitates; the latter is insoluble in hydrochloric acid, and therefore not merely occasioned by the water of the reagent. Red ferrocyanuret of potassium (sesqui), produces no precipitate. Hydrosulphuret of ammonia produces a red precipitate, soluble in excess of the precipitant. Sulphuretted hydrogen produces a red precipitate in acid and in neutral solutions of protoxide of antimony; if the solution is neutral, the precipitate does not fall till heat is applied, or hydrochloric acid added. Metallic zinc precipitates metallic antimony in the form of a black powder. Cadmium, iron, cobalt, tin, lead, bismuth, and copper, also throw down the metal. The compounds of protoxide of antimony, which are insoluble in water, are nearly all soluble in hydro-

was added to three quarts of boiling distilled water, which immediately became like milk; this was poured on a very bibulous filter, so that the liquor passed through before it had time to cool; and the white precipitate thus collected, being welledulcorated with boiling-water, and dried on a sand-bath, weighed 63 grains.

c. The washings were added to the filtrated liquor; and the whole was gradually evaporated at different times, between each of which it was suffered to cool, and remain undisturbed during several hours. A quantity of crystallized chloride of lead was thus obtained, until nearly the whole of the liquor was evaporated: to this last portion a few drops of sulphuric acid were added, and the evaporation was carried on to dryness; after which the residuum, being dissolved in boiling distilled water, left a small portion of sulphate of lead. The crystallized chloride of lead was then dissolved in boiling water; and, being precipitated by sulphate of soda, was added to the former portion, was washed, dried on a sand-bath, and then weighed 120·20 grains.

d. The filtrated liquor was now of a pale bluish green, which changed to deep-blue, upon the addition of ammonia; some ochraceous flocculi were collected, and, when dry, were heated with wax in a porcelain crucible, by which they became completely attractable by the magnet, and weighed 2·40 grains.

e. The clear blue liquor was evaporated nearly to dryness; and, being boiled with strong lixivium of pure

potash, until the whole was almost reduced to a dry mass, it was digested in boiling distilled water; and the black oxide of copper, being collected and washed on a filter, was completely dried, and weighed 32 grains.

200 grains of the ore, treated as here stated, afforded,

	Grains.
A. Sulphur	34
B. Oxide of antimony	63
C. Sulphate of lead	120·20
D. Iron	2·40
E. Black oxide of copper	32

But the metals composing this triple sulphuret are evidently in the metallic state; and antimony precipitated from hydrochloric acid by water, is to metallic antimony as 130 to 100; therefore, the 63 grains of that oxide must be estimated at 48·46 grains of the metal. Again, sulphate of lead is to metallic lead as 141 to 100; therefore, 120·20 grains of the former are = 85·24 grains of the latter. And, lastly, black oxide of copper contains 20 per cent. of oxygen, consequently, 32 grains of the black oxide are = 25·60 grains of metallic copper. The proportions for 200 grains of the ore will, therefore, be

Sulphur	34
Antimony	48·46
Lead	85·24
Iron	2·40
Copper	25·60
	<hr/>
	195·70
Loss	4·30

chloric acid, and sulphuretted hydrogen is the most unequivocal test. (H. ROSE.) Before the blowpipe, oxide of antimony is partly reduced in the exterior flame, and spreads a white smoke on the charcoal. In the interior flame it is readily reduced. With microcosmic salt and with borax it forms a hyacinth-coloured glass. Metallic antimony, when ignited on charcoal, becomes covered with acicular crystals of oxide. Sulphuret of antimony fuses upon charcoal, and is absorbed.

§ XVIII. BISMUTH.

THIS metal was first described by Agricola in 1529. It was sometimes called *Marcasite*. It is found *native*, and combined with oxygen, and with arsenic and sulphur. It is neither of common occurrence nor very abundant. *Native Bismuth* occurs crystallized in octoëdra and cubes, and generally contains arsenic, and sometimes cobalt. It has been found in Cornwall, and in Germany, France, and Sweden.

Bismuth is a brittle white metal with a slight tint of red: its specific gravity is 9.822. (HATCHETT, *Phil. Trans.*, 1803.) The specific heat of bismuth is 0.03084. It fuses at 476° (CRICHTON), 507° (RUDBERG), and always crystallizes on cooling. According to Chaudet, pure bismuth is somewhat flexible. A cast bar of the metal, $\frac{1}{10}$ of an inch diameter, supports, according to Muschenbroeck, a weight of forty-eight pounds. Bismuth is volatile at a high heat, and may be distilled in close vessels. It transmits heat more slowly than most other metals, perhaps in consequence of its texture, which is highly crystalline, as has been above shown. (See fig. 12, p. 113.) To obtain good crystals the bismuth requires to be purified by fusion with nitre, by which sulphur and arsenic, usually present in the metal as it occurs in commerce, are separated. When thus refined the metal is carefully fused, and poured into a heated mould; such as a common ingot, or a brass or iron mortar, where it is suffered slowly and quietly to cool. When the surface has solidified, the crust is pierced, and the liquid metal poured out from the interior: the mould is then suffered to cool, and the superior crust carefully removed, when the cavity is found lined with beautiful cubical crystals, usually highly iridescent, and having the exact form of common salt.

Sulphur, arsenic, and silver, are the usual impurities of bismuth: to separate these it may be dissolved in nitric acid, which leaves arseniate of bismuth; and hydrochloric acid added to the filtered solution throws down chloride of silver: hydrosulphuret of ammonia is then added in excess, by which sulphuret of bismuth is thrown down, and arsenic and sulphur remain in solution; the sulphuret is collected, washed, and reduced by fusion with a mixture of carbonate of soda and charcoal. (DUMAS.)

BISMUTH AND OXYGEN. PROTOXIDE OF BISMUTH. (*bi* + *o*) or Bi.—When bismuth is exposed to heat and air it oxidizes, forming a fusible *white oxide*. If the heat be increased by directing a current of oxygen upon the metal, it burns with much brilliancy, and produces an abundant yellow smoke, which condenses in the form of a yellowish-white sublimate. The readiest mode of obtaining oxide of bismuth, consists in dissolving bismuth in nitric acid, precipitating by dilution with water, edulcorating the precipitate, and heating it, when dry, to dull-redness.

At a red heat this oxide fuses into a brown liquid, and when in fusion it acts upon other oxides much in the same way as oxide of lead. It forms, on cooling, a yellow vitreous mass of a specific gravity of 8.2. It is easily reduced by hydrogen, charcoal, and several of the metals. It is decomposed by chlorine but not by iodine. It combines with water into a white pulverulent hydrate. The equivalent of bismuth, deduced from the experiments of J. Davy on the chloride, and of Lagerhielm on the oxide, is 72, (71 TURNER and GMEIN,) and the oxide consists of

		J. Davy. Lagerhielm: Klaproth.			
Bismuth	1	72	90	90	89.863
Oxygen	1	8	10	10	10.137
Oxide of bismuth	1	80	100	100	100.000

Native Oxide of Bismuth occurs, though very rarely; it has been found in Cornwall and Saxony: it is the *Bismuth Ochre* of some mineralogists.

PEROXIDE OF BISMUTH. SESQUIOXIDE OF BISMUTH. ($bi + \frac{1}{2}o$).—This oxide was first noticed by Bucholz and Brandes, but its nature and composition have been recently examined by A. Stromeyer. (TURNER.) It is formed when hydrate of potassa is fused with protoxide of bismuth, or by gently heating the protoxide in a solution of chloride of potassa or soda: after washing with water, any unchanged protoxide is dissolved by a solution of 1 part of pure nitric acid in 9 of water. It is a heavy brown powder; it is not salifiable: heated with sulphuric or phosphoric acid, oxygen is evolved, and sulphate or phosphate of the protoxide is formed: with hydrochloric acid, chlorine is evolved, and a protochloride produced. (*Ann. de Ch. et Ph.*, Li. 267.) According to Jacquelain (*Ann. de Ch. et Ph.*, LXvi. 113), the fusion of oxide of bismuth with potassa yields a bismuthate of potassa.

CHLORIDE OF BISMUTH ($bi + c$) is procured by gently heating the metal in chlorine; it burns with a blue flame, and forms a gray compound. This chloride may also be prepared by heating 2 parts of corrosive sublimate with 1 of powdered bismuth, and expelling the excess of the former and the mercury by heat; or by evaporating the solution of oxide of bismuth in hydrochloric acid to dryness, and heating the residue in close vessels. When nitrate of bismuth is decomposed by a solution of chloride of sodium, a white powder falls, which is either a *subchloride* or a compound of oxide of bismuth with the chloride. Chloride of bismuth was formerly called *Butter of Bismuth*. It is of a gray colour, and fuses at about 480° . In close vessels it does not sublime at a red heat. When exposed to air it deliquesces. It is decomposed by a large quantity of water, and yields a white deposit which is an *oxichloride*, containing, according to Dumas, 1 atom of chloride and 7 of oxide. Jacquelain obtained an oxichloride by directing steam into the fused chloride: he also describes double chlorides of bismuth and ammonia, potassa, soda, &c. (*Ann. de Ch. et Ph.*, LXvi. 125.) It consists of

		J. Davy.			
Bismuth	1	72	66.7	66.4	
Chlorine	1	36	33.3	33.6	
Chloride of bismuth	1	108	100.0	100.0	

CHLORATE OF BISMUTH has not been examined.

IODIDE OF BISMUTH ($bi + i$), obtained by heating iodine with the metal, is of a brown colour, and insoluble in water. When hydriodic acid or iodide of potassium is added to nitrate of bismuth, a precipitate falls of a deep-orange colour, insoluble in water, but soluble in liquid potassa.

IODATE OF BISMUTH ($Bi + i'$) is thrown down upon adding iodate of potassa to nitrate of bismuth. It is white, and insoluble. (PLEISCHL.)

BROMIDE OF BISMUTH ($bi + b$) is a gray compound, obtained by the direct action of bromine upon powdered bismuth. It fuses at about 400° , and sublimes at a low red-heat. It is decomposed by water, and oxide of bismuth is formed. (SERULLAS.)

FLUORIDE OF BISMUTH ($bi + f$) is soluble in water, and deposited, on evaporation, in the form of a white powder. (BERZELIUS.)

HYDRURET OF BISMUTH.—When bismuth is made the negative electrode in water, black dendritical crystals are deposited upon it. (RUHLAND, *Schweigger's Journal*, xv. 417.)

NITRATE OF BISMUTH. ($Bi + n$).—When nitric acid is poured upon powdered bismuth the action is intensely violent, and sometimes attended by ignition. Nitrate of bismuth is usually made by dissolving the metal to saturation in 2 parts of nitric acid and 1 of water: the action is rapid, and nitric oxide is copiously evolved: the solution affords deliquescent four-sided prismatic crystals, which are decomposed at a red heat, and leave oxide of bismuth. Ammonia occasions a precipitate in nitrate of bismuth, which is redissolved by excess of the alkali. Potassa and soda also throw down the oxide, which is but sparingly soluble in those alkalis. The crystals of nitrate of bismuth may be dissolved in a very small quantity of water, but if the solution, even when acid, be poured into a large quantity of water it is decomposed, and a fine white powder, called *magistery of bismuth*, *pearl white*, or *blanc de fard*, is precipitated, which is a *hydrated subnitrate of bismuth*. In this state it has been used in medicine as a tonic. (*Quarterly Journal*, viii. 295.) If characters be written on paper with nitrate of bismuth they are invisible when dry, but become white and legible on immersion in water, thus forming a *white sympathetic ink*. The same characters are rendered brown or black by solution of sulphuretted hydrogen. It is sometimes stated, that the salts of bismuth are blackened by exposure to light, but such an effect depends upon their containing a minute portion of silver. The *crystallized nitrate* is a hydrated salt, composed of

						Berzelius.
Oxide of bismuth	1	80	49.7	48.8		
Nitric acid	1	54	33.5	33.7		
Water	3	27	16.8	17.5		
Crystals of nitrate of bismuth	1	161	100.0	100.0		

The *subnitrate*, formed by the action of water on the nitrate, and dried at 212° , consists, according to Grouvelle (*Ann. de Ch. et Ph.*, xix. 138), of

						Grouvelle
Oxide of bismuth	4	320	81.6	81.37		
Nitric acid	1	54	13.8	13.97		
Water	2	18	4.6	4.66		
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Subnitrate of bismuth	1	392	100.0	100.00		

According to Phillips (*Trans. London Pharm.*), the preparation, as directed in the *London Pharmacopœia*, yields a trisnitrate (anhydrous), composed of

Oxide of bismuth	3	240	81.64
Nitric acid	1	54	18.36
<hr/>			
Trisnitrate of bismuth	1	294	100.00

SULPHURET OF BISMUTH (*bi*+*s*) is of a bluish colour and metallic lustre; it is less fusible than bismuth, and is reduced by hydrogen at a red heat, sulphuretted hydrogen being evolved. (H. ROSE.) When solutions of bismuth are decomposed by sulphuretted hydrogen, the black precipitate which falls is hydrated sulphuret of bismuth: when dried and heated it acquires its metallic lustre. Sulphuret of bismuth blends with, or is dissolved by, the fused metal in all proportions, but it again separates when the metal solidifies. It consists of

						H. Rose.
						<i>Native.</i>
						Lagerhielm.
						J. Davy.
Bismuth	1	72	81.8	81.619	81.8	80.98
Sulphur	1	16	18.2	18.381	18.2	18.92
<hr/>						
Sulphuret of bismuth	1	88	100.0	100.000	100.0	100.00

Native Sulphuret of Bismuth has been found in Cornwall, Bohemia, Saxony, and Sweden. It occurs massive and acicular, its lustre is metallic, and its colour bluish-gray: its density is 6.4. It is a very rare mineral.

HYPOSULPHITE OF BISMUTH has not been examined.

SULPHITE OF BISMUTH (*Bi*+*s*) is an insoluble white powder, which is not taken up by excess of the acid. (FOURCROY.)

HYPOSULPHATE OF BISMUTH has not been examined.

SULPHATE OF BISMUTH (*Bi*+*s'*) is obtained by dissolving the oxide in sulphuric acid and evaporating to dryness; or by heating powdered bismuth in sulphuric acid. It is a white compound, insoluble in, but decomposed by water, which converts it into a *subsulphate* and *super-sulphate*. The *sulphate* consists of

						Lagerhielm.
Oxide of bismuth	1	80	66.7	66.35		
Sulphuric acid	1	40	33.3	33.65		
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Sulphate of bismuth	1	120	100.0	100.00		

The *subsulphate* consists of

						Berzelius.
Oxide of bismuth	3	240	85.7	85.5		
Sulphuric acid	1	40	14.3	14.5		
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Subsulphate of bismuth	1	280	100.0	100.0		

PHOSPHURET OF BISMUTH (*bi+p*) does not, according to Pelletier, exist; at least, it cannot be formed by the usual process of projecting phosphorus upon the hot metal. When phosphuretted hydrogen gas is passed into nitrate of bismuth, a dark-brown precipitate ensues, which, heated in close vessels, loses the whole of its phosphorus.

Neither the *Hypophosphite*, nor *Phosphite*, have been examined.

PHOSPHATE OF BISMUTH is formed, according to Wenzel, by digesting the oxide in phosphoric acid; an insoluble subphosphate, and a soluble and crystallizable phosphate, are the results.

SELENIURET OF BISMUTH is a silver-white compound.

CARBONATE OF BISMUTH is thrown down from the nitrate by carbonated alkalis: it is a white powder, insoluble in water and in carbonic acid, and soluble in nitric acid with effervescence; when dried (in the air?) it consists, according to Thomson, of

Oxide of bismuth	3	240	83.0
Carbonic acid	1	22	7.6
Water	3	27	9.4
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Triscarbonate of bismuth	1		289		100.0

CYANURET OF BISMUTH has not been formed. *Ferrocyanuret* of bismuth, formed by double decomposition, is a white or yellowish powder, soluble in nitric acid, and precipitated again by water. (ITTNER.) The red ferrocyanuret (*ferrosesquicyanuret*) of potassium produces a brown precipitate in nitrate of bismuth.

BORATE OF BISMUTH is a white powder, insoluble in water.

ALLOYS OF BISMUTH.—Bismuth readily unites with *potassium*: Serullas obtains this alloy by heating together a mixture of 120 parts of bismuth, 60 of charred bitartrate of potassa, and 1 of nitre; these substances should be well rubbed together and fused in a covered crucible. The alloy decomposes water, and when broken and exposed to air, fuses, and even ignites. We know little of the other alloys of bismuth, excepting those which it forms with *tin* and *lead*, and which are remarkable for the low temperature at which they enter into fusion, and for the extraordinary irregularities of expansion and contraction which they exhibit with changes of temperature, and which have been particularly examined by Erman. An alloy of 2 parts of bismuth, 1 of lead, and 1 of tin, fuses at 200°. (ROSE.) The alloy of 8 parts of bismuth, 5 of lead, and 3 of tin, fuses at a little below 212°. The addition of 1 part of mercury renders it still more fusible, and this compound is sometimes cast for amusement into the form of tea-spoons, which run down when dipped into boiling water. It may also be employed for taking casts from medals, and even from the surface of wood and embossed paper: some beautiful casts have also been made in this metal of the internal ear, showing the complexities of its bony cavities.

Erman's experiments above alluded to, were made with Rose's fusible alloy (*Ann. de Ch. et Ph.*, XL. 197): the general results have already been adverted to under the head of "Expansion by heat" (p. 136). The following table, abridged from Erman, gives them more in detail:—

Temperature of the Alloy.		Volume of the Alloy.	Temperature of the Alloy.		Volume of the Alloy.
Reaum.	Fahr.		Reaum.	Fahr.	
0°	32°	100,000	60°	166°	99,389
10	54	100,192	65	178	99,478
20	76	100,443	70	180	100,000
30	99	100,803	75	201	100,862 fuses
35	111	100,830 max.	80	212	101,792
40	122	100,679	100	257	102,217
45	133	100,120	120	302	102,599
50	146	99,480	130	324	102,784
55	156	99,291 min.	140	346	103,072

CHARACTERS OF THE SALTS OF BISMUTH.—In the clear acid solutions of oxide of bismuth, potassa, soda, and ammonia, and their carbonates, produce white precipitates. Hydrosulphuret of ammonia and sulphuretted hydrogen produce brown or black precipitates, easily reduced to metallic bismuth when mixed with soda, and fused in the inner flame of the blow-pipe. Chloride and nitrate of bismuth are decomposed by the immersion of plates of zinc, cadmium, tin, iron, and lead: the metal is commonly thrown down in the form of a black crystalline powder, except by iron, which at first produces it with metallic lustre. Before the blowpipe, oxide of bismuth melts readily into a brown glass, which becomes brighter as it cools. With microcosmic salt it forms a gray-yellow glass, which loses its transparency, and becomes pale when cool: add a further proportion of oxide and it becomes opaque. With borax it forms a gray glass, which decrepitates in the interior flame, and the metal is reduced and volatilized. It is readily reduced by itself on charcoal.

§ XIX. URANIUM.

URANIUM was discovered by Klaproth in 1786, and named after the planet discovered by Herschel about the same time. Its ores are few and scarce. The *native phosphate* is contained in *Uranite*, or *Uranitic Mica*: the crystalline form of this mineral is the cube, and several modifications; it often occurs in thin quadrangular plates. It exhibits various shades of yellow and green. It has been found in France; and of great beauty near Callington, in Cornwall. The *ferriferous oxide of uranium* was formerly mistaken for an ore of zinc, and called *Pechblende*, till Klaproth demonstrated it to contain uranium. It is a compound of protoxide of uranium and iron, with lead, copper, and often other substances. From this ore uranium may be obtained by the following process:—Reduce it to powder, and expose it to heat in a muffle; then digest in nitric acid, diluted with 4 parts of water, taking care to employ excess of the mineral, by which the solution of the iron is nearly prevented. The nitric solution is filtered, and sulphuretted hydrogen passed through it to throw down lead and copper; the clear solution being poured off, is boiled, filtered, and evaporated, and crystals of nitrate of uranium are deposited: when these are heated they are decomposed, and at a red heat protoxide

of uranium remains. But the ore of uranium is often complicated by the presence of arsenic, and by silver, zinc, nickel, and cobalt, and does not contain more than 40 to 50 per cent. of oxide of uranium; in that case Arfwedson's process for the separation of the oxide may be resorted to, the details of which are given by Dumas (*Chimie appl. aux Arts*, iii. 454). It consists in dissolving the pulverized and roasted mineral in nitrohydrochloric acid, filtering, adding a little hydrochloric acid, and diluting the solution and passing sulphuretted hydrogen through it to throw down copper, lead, and arsenic, the sulphurets of which being separated by filtration, the clear liquor is boiled to expel sulphuretted hydrogen, and nitric acid added to peroxidize the iron, which is then thrown down by excess of carbonate of ammonia, together with earthy matters present, while the uranium, cobalt, and zinc, are retained in the filtered solution: this is then boiled to expel carbonate of ammonia; the precipitate is dried and ignited, by which the protoxide of uranium is rendered insoluble in acids; the other oxides therefore may now be removed from it by hydrochloric acid, and the protoxide of uranium remains in the form of a dark gray powder, which is to be well washed and dried.

Uranium was obtained, by Arfwedson, by passing hydrogen over the protoxide, heated in a glass tube; and by Berzelius, by heating the neutral oxalate of uranium in a close vessel, when it is resolved into carbonic acid and metallic uranium. It is crystalline, of a metallic lustre, of a gray-brown colour, brittle, and very difficult of fusion; its specific gravity has not been ascertained with precision; Bucholz states it as = 9.0. (GEHLEN'S *Journal*, iv.) Its specific heat is stated by Regnault to be 0.06190. Hitherto few experiments have been made upon this metal. It appears susceptible of two degrees of oxidizement, and its equivalent, deduced from the experiments of Arfwedson, Berzelius, and Schönberg, may be estimated at about 217. (217.26 GRAHAM.)

PROTOXIDE OF URANIUM ($urnm + o$) is obtained by strongly heating the pure perntrate, or by calcining the uraniate of ammonia in a close vessel. It is of greenish-gray colour, or green when in powder; when strongly heated it acquires a metallic appearance: it is infusible; it is very feebly acted on by the greater number of the acids, and the solutions and salts are green; nitric acid converts it into peroxide. When it is precipitated in the form of *hydrate*, by caustic potassa, it is more soluble, but, if boiled, it loses water, and becomes dark-coloured and difficultly soluble. When precipitated by carbonate of ammonia, it redissolves in excess of that precipitant, and forms a green solution. Protoxide of uranium consists of

				Schönberg.	Bucholz.	Arfwedson.	Berzelius.
Uranium	1	. 217	. 96.44	. 94	. 95.1	. 96.443	. 96.446
Oxygen	1	. 8	. 3.56	. 6	. 4.9	. 3.557	. 3.554
Protoxide of uranium	1	225	100.00	100	100.0	100.000	100.000

PEROXIDE OF URANIUM. SESQUIOXIDE OF URANIUM. URANIC ACID. ($urnm + 1\frac{1}{2}o$).—When a solution of nitrate of uranium is precipitated by caustic potassa, a yellow powder falls, which was regarded as a pure hydrated peroxide, but it always retains potassa, so that the peroxide of

uranium appears to act the part both of base and acid; if other precipitants are employed, they also are in part carried down by it, and the peroxide cannot thus be obtained pure. As thrown down by potassa, it is soluble in the carbonated alkalis, with which it forms double salts; and we are thus enabled to separate uranium from iron. Peroxide of uranium is not precipitated by sulphuretted hydrogen; a strong heat decomposes it, and converts it into protoxide: it is sometimes used to produce a deep-yellow upon porcelain. Arfwedson has shown that when the combinations of peroxide of uranium with baryta or with the oxides of iron, lead, or copper, are heated in a stream of hydrogen, water is formed; and the residue, cooled in hydrogen, takes fire on exposure to air.

The statements of different chemists respecting the composition of these oxides are much at variance. According to Thomson, the equivalent of uranium is 208, that of the protoxide 216, and of the peroxide 224; according to Berzelius and Arfwedson (*Ann. of Phil.*, N. S., ii.) the oxygen in the protoxide is to that in the peroxide as 1 to 1.5; hence the composition of the latter appears to be

				Arfwedson.	Schönberg.
Uranium	1	217	94.76	94.733	91.3
Oxygen	1½	12	5.24	5.267	8.7
Peroxide of uranium	1	229	100.00	100.000	100.0

The mineral called *Uranitic ochre* is generally considered as a *hydrated peroxide*.

CHLORIDES OF URANIUM.—When the hydrochloric solutions of the oxides of uranium are evaporated to dryness, and heated in a small retort, they lose water, and *chlorides* remain, which are readily soluble in water, alcohol, and ether. The ethereal solution of the perchloride, exposed to light, becomes dirty-green and turbid. These chlorides correspond in composition with the oxides.

POTASSA-PERCHLORIDE OF URANIUM crystallizes from its concentrated solution, and forms a triple salt, soluble in alcohol.

The action of *iodine* and *fluorine* upon uranium has not been examined.

BROMIDE OF URANIUM is formed by boiling uranium and bromine in water, or by dissolving the peroxide in hydrobromic acid: it may be crystallized in flat yellow prisms, which are very deliquescent, and of a styptic taste; it is decomposed at a high heat, and oxide of uranium remains.

NITRATE OF URANIUM, formed as above directed, yields yellow prismatic and tabular crystals, very soluble, and somewhat deliquescent in a moist air. They are also readily soluble in alcohol and ether, and when the latter solution is exposed to light, it is decomposed, becomes green, and deposits the protoxide. They consist of

				Bucholz.	Brande.
Peroxide of uranium	1	229	62.91	61	60.7
Nitric acid	1½	81	22.25	25	39.3
Water	6	54	14.84	14	
Crystals of nitrate of uranium	1	364	100.00	100	100.0

SUBNITRATE OF URANIUM, upon the authority of Bucholz, is formed by heating the nitrate, which renders a part insoluble in water, and separates in the form of a yellow powder.

AMMONIO-NITRATE OF URANIUM is a yellow crystallizable salt.

SULPHURET OF URANIUM was obtained by Rose, by passing the vapour of sulphuret of carbon over the protoxide, at a high heat. The alkaline hydrosulphurets form black precipitates in the pure solutions of uranium.

PROTOSULPHATE OF URANIUM forms green prismatic crystals: it may be formed by boiling the protoxide in sulphuric acid. With sulphate of potassa it produces a triple salt.

PERSULPHATE OF URANIUM forms yellow prismatic crystals, decomposable by heat, and, according to the analysis of Bucholz, consisting of 70 oxide, 18 acid, 12 water, = 100. Its alcoholic solution becomes ethereal and green when exposed to the sun's rays, and deposits a precipitate, which is a subsulphate of the protoxide. According to John, these sulphates are occasionally found *native*. (*Ann. of Phil.*, viii. 390, 2nd series.

POTASSA-PERSULPHATE OF URANIUM.—When a mixture of persulphate of uranium and sulphate of potassa is evaporated to crystallization, yellow granular crystals are obtained, composed, according to Berzelius, of

Potassa	3	144	16.57
Peroxide of uranium	2	458	52.70
Sulphuric acid	6	240	27.62
Water	3	27	3.11
Potassa-persulphate of uranium	1	869	100.00

PHOSPHURET OF URANIUM has not been examined.

PERPHOSPHATE OF URANIUM is thrown down by phosphoric acid from the *peracetate*: it is a difficultly-soluble yellow salt: it is soluble in excess of phosphoric acid, and in carbonate of ammonia. (LAUGIER, *Ann. de Ch. et Ph.*, xxiv. 239.) It exists *native* in the micaceous ore of uranium. It consists of

Peroxide of uranium	1	229	62.91	Laugier.
Phosphoric acid	$1\frac{1}{2}$	54	14.84	16.6
Water	9	81	22.25	22.0
Hydrated perphosphate of uranium	1	364	100.00	99.6

The *Uranite of Autun* is a hydrated double phosphate of peroxide of uranium and lime.

PERCARBONATE OF URANIUM is precipitated by a carbonated alkali from the solutions of the peroxide, but it loses carbonic acid on drying.

CYANURET OF URANIUM is thrown down in the form of a yellow powder, by solutions of cyanuret of potassium.

FERROCYNANURET OF URANIUM is thrown down in the form of a rich brown and very characteristic precipitate: in colour, it much resembles the ferrocyanuret of copper.

CHARACTERS OF THE SALTS OF URANIUM.—The *protosalts* of uranium have a green, and the *persalts* a yellow colour, and an astringent metallic taste. Potassa forms in the solutions of the latter a yellow precipitate, and carbonate of potassa a straw-coloured precipitate: both these precipitates are insoluble in excess of pure alkali, but dissolve in the alkaline carbonates. Ferrocyanuret of potassium and tincture of galls produce brown precipitates in solutions of uranium. The salts are mostly soluble in alcohol and in ether, and these solutions acquire a green colour by exposure to the sun. The protosalts have been little examined. Uranium is not precipitated from its solutions by sulphuretted hydrogen, nor is it thrown down in a metallic state by any of the other metals. Before the blowpipe the peroxide of uranium becomes green or greenish-brown. With microcosmic salt in the interior flame it forms a clear yellow glass, the colour of which becomes more intense when cold. If long exposed to the exterior flame, and frequently cooled, it gives a pale yellowish-red or brown glass, which becomes greenish as it cools. With borax in the interior flame, a clear, colourless, or faintly-green glass is formed, containing black particles, which appear to be the metal in its lowest state of oxidation. In the exterior flame this black matter is dissolved, if the quantity be not too great, and the glass becomes bright yellowish-green, and after further oxidation yellowish-brown. If brought again into the interior flame, the colour gradually changes to green, and the black matter is again precipitated, but no further reduction takes place.

§ XX. TITANIUM.

TITANIUM was first recognised as a distinct substance by Mr. Gregor, in 1791; he detected it in a mineral found in the form of a black sand in the vale of Menachan, in Cornwall. Some of its compounds were afterwards examined by Klaproth, in 1795, who named it *Titanium*, after the Titans of ancient mythology. (See his Analysis of the Red Schorl of Hungary, *Beiträge*, i. 233.) For our knowledge of the properties of *Titanium* in its metallic state we are chiefly indebted to Dr. Wollaston, who discovered it in small cubic crystals, having the lustre of burnished copper, in the slag of the iron-furnaces at Merthyr Tydvil, in South Wales. (*Phil. Trans.*, 1823, p. 17.) These crystals, which have been found in similar slags from other sources, are titanium, almost absolutely pure. They have the following properties:—They are so hard as to scratch rock-crystal; they are not acted on by nitric, hydrochloric, or sulphuric acids, nor are they soluble in nitrohydrochloric acid. Before the blowpipe they are infusible; they are, however, superficially oxidized by a continued heat, becoming of a purple or red colour. Borax has no action on them, but only removes the superficial oxide. Nitre oxidizes them on the surface. The combined action of nitre and borax soon effects their solution; but as these salts do not unite by fusion, the addition of soda accelerates their action. The fused mass becomes opaque on cooling, by the deposit of a white oxide, which may either be previously freed of the salts by boiling-water, and then dissolved in hydrochloric acid, or the whole mass may be at once dissolved together. In either case alkalis precipitate from the solution a white oxide, insoluble in

excess of alkali, either pure or carbonated. By evaporating the hydrochloric solution to dryness at 212° , it is freed of redundant acid, and a soluble chloride remains, in a favourable state for exhibiting the characteristic properties of the metal.

Titanium exists in the state of oxide in the minerals called *Titanite* and *Menachanite*. *Titanite* is a nearly pure oxide of titanium; it is of a brown colour, and occurs imbedded in the quartz and granite of primitive countries, and sometimes traverses rock-crystals in fine hair-like filaments. In this country, it occurs at Beddgelert, in Caernarvonshire; and near Killin, in Scotland. The finest specimens are those from the vicinity of Mont Blanc and St. Gothard. The mineral, known by the name of *anatase*, *octoëdrite*, and *oysanite*, is nearly of the same nature as titanite. It is found in Bavaria, Norway, Switzerland, and in the valley of Oysans, in France. *Menachanite* consists principally of oxides of titanium and iron; it is found in small grains, somewhat resembling coarse gunpowder, in the bed of a small stream at Menachan, in Cornwall. *Nigrine*, *iserine*, *rutilite*, and *sphene*, are also ores of titanium.

According to Laugier (*Ann. de Chim.*, LXXXIX. 306), the metal may be obtained from *titanite* by fusion with potassa; the fused mass, washed with water, leaves oxide of titanium, containing a little iron; it is to be dissolved in hydrochloric acid, and precipitated by oxalic acid. The oxalate affords the metal by intense ignition with charcoal: it is, however, not possible to obtain it in any state of agglutination. From *menachanite*, white oxide of titanium may be obtained by fusing it with potassa, and adding hydrochloric acid to the alkaline solution, so as merely to neutralize the alkali and precipitate the oxide; to separate a little adhering iron, this must be dissolved in excess of hydrochloric acid, and precipitated by oxalic acid as before.

Liebig prepares metallic titanium by putting fragments of recently-made ammonio-chloride of titanium into a glass tube, half an inch wide and two or three feet long, transmitting through it a current of perfectly dry ammonia, and, when atmospheric air is entirely displaced, applying heat until the glass softens: complete decomposition ensues, nitrogen gas is disengaged, hydrochlorate of ammonia sublimes, and metallic titanium is left in the state of a dark blue-coloured powder. If exposed to the air while warm, it is apt to take fire. (TURNER.)

The equivalent of titanium has not been very satisfactorily determined; Gmelin adopts 31, Dr. Turner 24.3, Dr. Thomson 26; I have assumed 24, as the whole number, which, according to Dr. Turner, is most consistent with the experimental results of Rose.

PROTOXIDE OF TITANIUM.—Titanium appears to be susceptible of two degrees of oxidizement. The mineral called *anatase* is regarded as the *protoxide*, but its composition has not been determined with accuracy. When peroxide of titanium is intensely heated with charcoal, or when a plate of zinc is immersed in a solution of chloride of titanium, a purple powder is obtained, which appears to be the protoxide: it is also formed when the vapour of potassium is passed over heated titanous acid; it is infusible and unchanged by heat alone, but when exposed to the joint action of heat and air it passes slowly into titanous acid. It is very

sparingly soluble in hydrochloric acid, which yields a blue solution: boiling sulphuric acid dissolves it more copiously, and the solution, when saturated, is deep blue: it forms a double salt with ammonia; boiled with nitric or nitrohydrochloric acid it is converted into titanous acid. It probably consists of

Titanium	1	24	75
Oxygen	1	8	25
<hr/>					
Protoxide of titanium	1		32		100

PEROXIDE OF TITANIUM. TITANIC ACID ($ti+2o$) may be obtained from *rutile*, by fusing it in fine powder, in a platinum crucible, with thrice its weight of pure carbonate of potassa: a gray mass is obtained, which, after having been washed with water, is dissolved in hydrochloric acid, and on diluting with water, and boiling the solution, the greater part of the peroxide of titanium is precipitated; it is collected, and washed with very dilute hydrochloric acid. In this state it still is apt to retain traces of iron and manganese, which may be separated by digesting the moist precipitate with hydrosulphuret of ammonia, which forms sulphurets with the iron and manganese, but does not affect the oxide of titanium: dilute hydrochloric acid removes the sulphurets, and the oxide of titanium, after being again washed and heated red-hot, is pure. (ROSE, *Ann. de Ch. et Ph.*, xxiii.)

Titaniferous Oxide of Iron, which is more abundant than *rutile*, may also be used as a source of titanium; it is pulverized, washed, and exposed at a high red-heat in a porcelain tube to the action of a current of dry sulphuretted hydrogen, as long as water is evolved: the oxide of iron is converted into sulphuret, but the oxide of titanium undergoes no change: the product, when cold, is digested in hydrochloric acid, which leaves titanous acid mixed with sulphur, from which it may be freed by heat; but as it still retains some iron, it must be again subjected to the action of the current of sulphuretted hydrogen in the porcelain tube; if afterwards treated by hydrochloric acid, well washed, and ignited, it is white and pure. (ROSE, *Ann. de Ph.*, lxxxviii., and *Ann. de Ch. et Ph.*, xxxviii. 131.)

This oxide of titanium is white, and very infusible, and difficult of reduction: when recently precipitated it dissolves in some of the acids, but becomes nearly insoluble after it has been ignited. Its solution in hydrochloric acid is always very sour, and part of the oxide falls down when it is heated to the boiling point, but by careful evaporation to dryness, a soluble chloride remains. It is precipitated by the pure and carbonated alkalis; infusion of galls and ferrocyanuret of potassium throw it down of a characteristic red colour. When a rod of zinc is immersed in the hydrochloric solution of peroxide of titanium, a purple precipitate (probably of the protoxide) is obtained. The recently-precipitated peroxide is with difficulty separated from water upon a filter, but passes through in a milky state; the addition of a little acid or alkali facilitates its separation. It seems doubtful whether this oxide forms any definite salts with the acids: it unites with bases, and has thence been termed *titanous acid*. There are many resemblances between this oxide and the peroxide of tin. It consists of

					H. Rose.	
Titanium	1	24	60	61		
Oxygen	2	16	40	39		
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Titanic acid	1	40	100	100		

BICHLORIDE OF TITANIUM ($ti+2c$) was obtained by Mr. George (*Annals of Phil.*, N. S., ix. 18), by passing dry chlorine over metallic titanium, heated to redness. It is a dense, transparent, and colourless fluid, fuming when exposed to air. It boils at a little above 212° , and acts violently upon water, evolving chlorine, and furnishing, when the water is not in excess, a white salt, very soluble, and deliquescent. The density of its vapour is, according to Dumas (*Ann. de Ch. et Ph.*, xxxiii. 388), 6.836, and considering 1 volume of this vapour as composed of 1 volume of titanium vapour, and 2 volumes of chlorine, he deduces the equivalent of titanium = 26.4. When this chloride is exposed to ammoniacal gas it absorbs it, and becomes solid, forming the compound from which Liebig, as above stated, obtained metallic titanium. It absorbs phosphuretted hydrogen, and forms a dry brown powder, which, when heated, yields a yellow sublimate, in which 3 atoms of the bichloride are combined with 1 of phosphuretted hydrogen. (ROSE.) It also forms crystallizable double salts with the alkaline chlorides. Assuming this to be a *bichloride*, it consists of

					H. Rose.	
Titanium	1	24	25	25.5		
Chlorine	2	72	75	74.5		
<hr/>						
Bichloride of titanium	1	96	100	100.0		

BIFLUORIDE OF TITANIUM.—The peroxide of titanium readily dissolves in hydrofluoric acid. When this solution is saturated with potassa and evaporated, a *titanofluoride of potassium* is the result, composed, according to Berzelius, of 1 atom of bifluoride of titanium + 1 atom of fluoride of potassium. Many other protoxides may be substituted for potassa; and hence the class of double salts which have been termed *titanofluorides*.

BISULPHURET OF TITANIUM was obtained by Rose, by passing the vapour of sulphuret of carbon over peroxide of titanium. It has a dark-green colour and metallic lustre. It burns with a bluish flame into sulphurous and titanous acid; it is readily attacked by nitric and nitrohydrochloric acid, and when boiled in solution of potassa or of soda, sulphurets and titanates of the alkaline bases are formed. (*Quarterly Journal*, xvi. 97.) It is stated to consist of

Titanium	1	24	42.9
Sulphur	2	32	57.1
<hr/>			
Bisulphuret of titanium	1	56	100.0

PHOSPHURET OF TITANIUM is formed, according to Chenevix, by heating the phosphate with charcoal; it has a white metallic lustre, and is brittle.

PHOSPHATE OF TITANIUM falls when phosphoric acid is added to solution of peroxide of titanium in hydrochloric acid, in the form of a bulky white precipitate, which dries into a gummy mass. (H. ROSE.)

TITANIATE OF POTASSA.—The peroxide of titanium may be united by fusion with several bases, forming a class of compounds which have been termed *Titaniates*. When thus fused with potassa it yields a compound, from which water abstracts potassa, and leaves a white powder, composed of 18 potassa + 82 peroxide of titanium, and which is soluble in hydrochloric acid. (H. ROSE.)

CHARACTERS OF THE SALTS OF TITANIUM.—Titanium is not thrown down in the metallic state by any other metal. The bulky red precipitate which its solutions afford with infusion of galls, is very characteristic; the other properties of its compounds will be evident from the preceding paragraphs. Before the blowpipe, oxide of titanium becomes yellowish when ignited in a spoon, and upon charcoal dark-brown. With microcosmic salt it gives in the interior flame a fine violet-coloured glass, more tending to blue than that from manganese. In the exterior flame this colour disappears. With borax it gives a dirty hyacinth colour.

§ XXI. CERIUM.

THIS metal, which is named after the planet Ceres, was obtained, in 1803, by Hisinger and Berzelius, from a mineral found at Bastnas in Sweden, to which they have given the name of *cerite*. It was originally, in consequence of its density, called *heavystone* (schwerstein), and was considered by Klaproth as containing a peculiar earth, which he called *ochroit*. Cerium also occurs in *gadolinite*, and several other minerals of Fahlun; and in *orthite*, which is not an uncommon ingredient of Scandinavian granite. It is also contained in *Allanite*, a mineral from Greenland, first distinguished as a peculiar species by Mr. Thomas Allan, of Edinburgh: it contains, according to Dr. Thomson's analysis, about 40 per cent. of oxide of cerium.

To obtain cerium, the ore is calcined, pulverized, and digested in nitrohydrochloric acid. To the filtered solution, from which part of the excess of acid has been boiled off, oxalic acid is added, which occasions a white precipitate: this, when dried and ignited, is *peroxide of cerium*, but it is extremely difficult of reduction. Mr. Children succeeded in fusing it by the aid of his powerful Voltaic apparatus, and when intensely heated it burned with a vivid flame, and was partly volatilized. Vauquelin describes cerium as a hard white brittle metal, (*Ann. de Chim.*, iv.,) and as only soluble in nitrohydrochloric acid. Mosander obtained it by heating the dry chloride with potassium; violent action ensues, and a gray alloy of cerium and potassium results, which evolves hydrogen when put into water, and leaves the cerium in the form of a gray metallic powder, which, when dried and heated, burns brilliantly into an oxide, and is soluble in the weakest acids with the evolution of hydrogen. The equivalent of cerium may be assumed as 48. (46 GMELIN and TURNER.)

PROTOXIDE OF CERIUM ($Ce + O$) or Ce , is white, and may be obtained by precipitation from its chloride: it forms salts with the acids, from which the alkalis throw down a white hydrate; the carbonated alkalis, a white carbonate, soluble in excess of the precipitant; and oxalate of ammonia a white oxalate.

Berzelius obtains protoxide of cerium as follows:—Cerite (composed according to Hisinger of 68·6 oxide of cerium, 18 silica, 1·25 lime, 2 oxide of iron, and 9·75 water,) is boiled in nitrohydrochloric acid, and the solution evaporated to dryness. The residue, after having been gently heated, is again dissolved in water, and the solution precipitated by benzoate of ammonia, which throws down the iron: the remaining solution is precipitated by caustic ammonia, and the precipitate (which is a mixture of the oxides of cerium) dissolved in hydrochloric acid, evaporated to dryness, and heated to redness in a retort as long as it smells of chlorine. The residuary salt is dissolved in water and precipitated by caustic potassa. This precipitate, which is *hydrated protoxide of cerium*, presently becomes yellow by exposure to air, and cannot be obtained free from water, for all attempts to dry it are attended by its partial peroxidizement. Protoxide of cerium consists of

Cerium	1 . . .	48 . . .	85·7 . . .	Hisinger. 85·19
Oxygen	1 . . .	8 . . .	14·3 . . .	14·81
Protoxide of cerium	1	56	100·0	100·00

SUPEROXIDE OF CERIUM? (*Ceroxyd-oxidul* of Berzelius) is obtained by subjecting the peroxide of cerium at a red heat to the action of hydrogen gas; or by subjecting the oxalate or carbonate of the protoxide of cerium to a white heat. It is a lemon-yellow powder, soluble in hydrochloric acid with the evolution of chlorine, and which, when heated in the air, becomes peroxide. It has not been analyzed.

PEROXIDE OF CERIUM; SESQUIOXIDE OF CERIUM. ($Ce + 1\frac{1}{2}O$).—When protonitrate of cerium is decomposed at a red heat, or when protocarbonate of cerium is heated in the air, this oxide is obtained in the form of a red powder. It is soluble in the acids, and when acted on by hydrochloric acid, it evolves chlorine: these solutions, when decomposed by potassa, afford a bulky precipitate of *hydrated peroxide of cerium*; it is pale-yellow when moist, dark-yellow when dried. Ammonia generally throws down *subsals* from these solutions. The moist hydrate is insoluble in the caustic alkalis. This oxide consists of

Cerium	1 . . .	48 . . .	80 . . .	Hisinger. 79·31
Oxygen	$1\frac{1}{2}$. . .	12 . . .	20 . . .	20·69
Peroxide of cerium	1	60	100	100·00

CHLORIDE OF CERIUM. ($Ce + Cl$).—When the solution of the protoxide in hydrochloric acid is evaporated to dryness, a deliquescent *protochloride* is obtained, which is readily soluble in water and in alcohol; the latter solution burns with a green sparkling flame. The peroxide of cerium also dissolves in hydrochloric acid, furnishing a brown solution; but when it is gently heated chlorine is evolved, and a protochloride formed. Chloride of cerium consists of

Cerium	1 . . .	48 . . .	57·1
Chlorine	1 . . .	36 . . .	42·9
Protochloride of cerium	1	84	100·0

BROMIDE OF CERIUM is uncrystallizable and very deliquescent: by heat it is converted into an *oxibromide*.

FLUORIDE OF CERIUM (*ce + f*) is an insoluble yellow powder; it has been found *native* in the mines of Fahlun, in Sweden; and it exists in the mineral called *yltrocrite*, combined with the fluorides of yttrium and of calcium. 100 parts of this mineral from Finbo contain 22 fluoride of cerium, 11 fluoride of yttrium, 67 fluoride of calcium.

SULPHURET OF CERIUM may be obtained, according to Mosander, by passing the vapour of sulphuret of carbon over red-hot carbonate of cerium; or by fusing oxide of cerium with excess of sulphuret of potassium, and removing the soluble parts by washing with water. It is an orange-coloured compound, and appears to consist of

Berzelius.							
Cerium	.	.	.	1	.	48	75
Sulphur	.	.	.	1	.	16	25
				1		64	100
Sulphuret of cerium				1		64	100

HYPOSULPHATE OF CERIUM, formed by spontaneous evaporation of a solution of protocarbonate in hyposulphuric acid, crystallizes in delicate colourless prisms containing 42.79 of protoxide per cent.

PROTOSULPHATE OF CERIUM may be obtained by digesting the protocarbonate in dilute sulphuric acid: it yields small crystals, of a purplish tint, and difficultly soluble in water.

PERSULPHATE OF CERIUM is a lemon-yellow salt, from which a red heat expels half the acid, and converts it into a red *subpersulphate*. It is obtained by digesting peroxide of cerium in sulphuric acid, diluted with 4 parts of water: it has an acid and sweetish taste.

PROTOSULPHATE OF CERIUM AND POTASSA.—This double salt is obtained when solid sulphate of potassa is added to a solution of a protosalt of cerium: as it dissolves, a white powder falls, which is the potassa-sulphate of cerium, and in this way, by using excess of sulphate of potassa, the whole of the cerium is thrown down: the double salt, though soluble in water, is insoluble in solution of sulphate of potassa. It is deposited from its solution in boiling water in small crystals of a pale amethyst colour. At a red heat it fuses, but is not decomposed: the alkalis throw down a basic salt from its solution, which can only be perfectly decomposed by long digestion in excess of alkali. This is the most characteristic salt of cerium, and it serves to separate the oxide of cerium, in analytical operations. (BERZELIUS.)

PHOSPHURET OF CERIUM has not been obtained.

PROTOPHOSPHATE OF CERIUM is an infusible white powder, somewhat soluble in hydrochloric and nitric acids, but insoluble in excess of phosphoric acid.

CARBURET OF CERIUM is obtained, according to Mosander, by heating the oxalate in a retort: a mixture of peroxide and of carburet remains, which when digested in hydrochloric acid leaves the pure carburet: it is

dark-brown, heavy, and insoluble in the acids; heated in the air it burns into peroxide.

PROTOCARBONATE OF CERIUM is precipitated by the carbonated alkalis, in the form of a white powder, insoluble in water and in excess of carbonic acid. It is decomposed by a strong heat, and if exposed to air, peroxide of cerium remains, but if air be excluded, the superoxide (*oxyd-oxydul*) remains. (HISINGER and BERZELIUS.) It has been found *native*. When protoxide of cerium is exposed to air it gradually absorbs carbonic acid.

PERCARBONATE OF CERIUM much resembles the protocarbonate in appearance, but it is heavier and of a less pure white colour.

The remaining combinations of cerium, with the exception of some of its triple salts, have not been examined.

CHARACTERS OF THE SALTS OF CERIUM.—The *protosalts* of cerium are colourless, or slightly purple, of a sweet and astringent taste, and bear much general resemblance to the salts of yttrium. They are unaltered by infusion of galls and by sulphuretted hydrogen, but are precipitated by the hydrosulphuretted alkalis. Ferrocyanuret of potassium occasions in them a white precipitate. The salts of the *peroxide* are of a yellow colour, and the hydrosulphurets occasion in them a white precipitate: they are precipitated as above stated by sulphate of potassa. None of the other metals precipitate cerium in a metallic state.

Before the blowpipe the oxide of cerium becomes red-brown when ignited. When the proportion is small, it forms with the fluxes a clear, colourless glass, which by increasing the proportion of oxide becomes yellowish-green while hot. With microcosmic salt, if heated a long time in the internal flame, it gives a clear colourless glass. With borax under similar circumstances, it gives a faint yellow-green glass while warm, but is colourless when cold. Exposed again for some time to the external flame, it becomes reddish-yellow, which colour it partly retains when cold. If two transparent beads, one of the compound with microcosmic salt, the other with borax, be fused together, the triple compound becomes opaque and white.

§ XXII. LANTANUM.

It has been ascertained by Mosander that the minerals containing cerium, contain also another metallic oxide, which, as it has hitherto lain concealed in oxide of cerium, he designates *Lantanum* (*λανθάνειν*, *to lurk*). It is probable, therefore, that the preceding details respecting cerium will require revision, as the oxide of lanthanum has in most, if not in all cases, been present in the oxides and salts supposed to be those of pure cerium. To separate these oxides, their mixture is dissolved in nitric acid, evaporated to dryness, and the residue exposed to a red heat; it is then digested in very dilute nitric acid (1 of acid to 100 of water), which dissolves the oxide of lanthanum and leaves that of cerium; the former may be thrown down in the form of a carbonate by a carbonated

alkali; when ignited it acquires a dirty red hue, and in hot water becomes a white hydrate; it dissolves in a solution of hydrochlorate of ammonia with the gradual expulsion of ammonia. The salts of the oxide of lantanium are astringent, but not sweet; their crystals generally have a reddish tint, and their solutions, when free from cerium, are not precipitated by the addition of sulphate of potassa.

§ XXIII. TELLURIUM.

IN the year 1782, Müller, of Reichenstein, showed that certain Transylvanian gold ores contained a new and distinct metal, and his experiments were verified by Klaproth in 1798, who named this new metal *Tellurium* (from *tellus*, the earth).

The ores of tellurium are, 1. *Native*, in which the metal is combined with iron and a little gold. 2. *Graphic ore*, which consists of tellurium, gold, and silver. 3. *Yellow ore*, a compound of tellurium, gold, lead, and silver; and 4. *Black ore*, consisting of the same metals with copper and sulphur. 5. *Bismuthic Tellurium*. These ores have only been found in the Transylvanian mines, in Siberia, and in Hungary.

The metal is extracted from them by precipitating their diluted nitrohydrochloric solution by potassa, which is added in excess, so as to redissolve the precipitate: the clear liquor is then poured off, and saturated with hydrochloric acid, which affords a precipitate of oxide of tellurium. This, heated in a glass retort with one-tenth its weight of charcoal, furnishes the metal, part of which sublimes.

Tellurium is of a bright gray colour, brittle, easily fusible, and volatile. Its specific gravity is 6.1 to 6.3. Its specific heat, as determined by Regnault, is 0.05155. It is easily crystallizable, and, for a metal, it is a bad conductor of heat and electricity; indeed, several of its metallic characters are imperfect, and it may be said to form a kind of connecting link between sulphur or selenium and the metals, as far as its general habits are concerned.

OXIDE OF TELLURIUM. TELLUROUS ACID. (*tel* + *o*) or **TEL.**—Exposed to heat and air, tellurium readily burns, exhaling a peculiar odour, which Berzelius ascribes to selenium, and forming a yellowish-white oxide, consisting, according to Klaproth (*Beitrag*e, vol. iii.), of tellurium 100 + oxygen 20.5. Oxide of tellurium is also obtained by evaporating the nitrate to dryness, and exposing the residue to a dull red-heat. If it be precipitated from its solutions by alkalis, it generally retains a portion of the precipitant.

Dr. Turner adopts, as the result of the latest experiments of Berzelius, the number 64.2 as the equivalent of tellurium, and considers the present oxide as constituted of 1 equivalent of the metal + 2 of oxygen. (*Poggend.*, xviii. 392.) Consistently with our equivalents, it is a protoxide consisting of

				Berzelius.	Klaproth.
Tellurium	1	32	80	80.11	83.14
Oxygen	1	8	20	19.89	16.86
Oxide of tellurium	1	40	100	100.00	100.00

PEROXIDE OF TELLURIUM. TELLURIC ACID. (*tel* + 14 *o*) or *TEL*.—When the above oxide is deflagrated with nitre, it is converted, according to Berzelius, into telluric acid: this compound may also be obtained by passing chlorine through the solution of the oxide in potassa till it is fully saturated: slight excess of nitric acid, and a little chloride of barium, are then added to separate any accidental traces of sulphuric or of selenic acids; the filtrated liquor is neutralized by ammonia, and chloride of barium added, which occasions a precipitate of *tellurate of baryta*; this, digested with a fourth of its weight of sulphuric acid (diluted with water), yields a solution, which, when filtered and carefully evaporated, yields crystallized *hydrated telluric acid*, from which adhering sulphuric acid may be removed by alcohol. This hydrate loses its water by heat, and the *anhydrous acid*, of a lemon-yellow colour, remains, constituted, according to Berzelius, of

Tellurium	1	32	72.73
Oxygen	1½	12	27.27
<hr/>					
Telluric acid	1		44		100.00

CHLORIDE OF TELLURIUM is a white fusible compound, formed by heating the metal in chlorine. According to Davy (*Elements*, p. 410), it consists of 2 tellurium + 1.85 chlorine; but his experiments were made upon a very limited quantity of materials. The solution of oxide of tellurium in hydrochloric acid is precipitated as a subsalt by water; excess of water redissolves it. Rose has described a *bichloride* (*Poggend.*, xxi. 443), and, according to him, these chlorides form violet vapours, which condense, the one into a black, the other into a white, solid.

IODIDE OF TELLURIUM.—Iodine readily combines with tellurium, forming a deep-brown compound, which dissolves in water.

TELLURIUM AND HYDROGEN.—When tellurium is negatively electrized in contact with water, a brown powder is produced, which has been described as a solid *hydruret*, but which, according to Dumas, is only finely divided tellurium. When an alloy of tellurium and tin is acted on by hydrochloric acid, *telluretted hydrogen gas* is evolved; it reddens litmus, dissolves in water, and possesses the general habitudes of sulphuretted hydrogen. According to Berzelius, telluretted hydrogen gas contains 2.99 per cent. of hydrogen; it must therefore consist of

Tellurium	1	32	97.1
Hydrogen	1	1	2.9
<hr/>					
Telluretted hydrogen gas	1		33		100.0

SULPHURETS OF TELLURIUM.—There appear to be two sulphurets of tellurium, which, according to Berzelius, act as *sulphur-acids*; they are obtained by the decomposition of tellurous and telluric acids by sulphuretted hydrogen.

THE SALTS OF TELLURIUM are decomposed by the alkalis, and the precipitate is redissolved when they are added in excess. Hydrosulphuret of ammonia forms a brown precipitate; ferrocyanuret of potassium occasions

no change. Zinc, lead, tin, copper, cadmium, or iron, immersed into the solutions, cause the separation of metallic tellurium; it generally appears as a black powder, which acquires lustre by friction.

The oxides (or acids) of tellurium combine with many of the metallic oxides, and produce a class of compounds which have been called *tellurites* and *tellurates*.

TELLURATE OF POTASSA may be formed by heating oxide of tellurium with nitre, and redissolving the residuum in boiling water, which, on cooling, deposits an imperfectly-crystallized white powder, difficultly soluble in water. The tellurates of the alkaline earths, and many of the metallic oxides, are insoluble.

§ XXIV. ARSENIC.

THE distinct metallic characters of this substance were first noticed by Brandt, in 1733; but it was probably known to Paracelsus, and a process for obtaining it is given by Schroeder, in 1649. Its general chemical relations are such as to place it rather among the simple acidifiable substances than among the metals, for it forms no salifiable base with oxygen, but constitutes *acids*: it, however, has the lustre and opacity of a metal, and conducts electricity.

Arsenic may be obtained from the purified *white arsenic* of commerce, by mixing it with its weight of *black flux*, and introducing the mixture into a Florence flask or small retort, placed in a sand-bath, gradually raised to a red heat: a brilliant metallic sublimate of pure arsenic collects in the upper part of the flask or in the neck of the retort. The volatility of white arsenic prevents its easy reduction by charcoal alone; but the potassa in the flux enables it to acquire a temperature sufficient for its perfect reduction. Arsenic may also be obtained by heating the ore called *native arsenic* (scherbenkobalt of the Germans) in coarse powder in a retort; the metal sublimes, leaving the impurities behind.

Arsenic is of a steel-gray colour, crystalline texture, quite brittle, and of a specific gravity = 5.7 to 5.9. Its specific heat, as ascertained by Regnault, is 0.08140. It readily volatilizes, and in close vessels may be sublimed at a temperature of 360°, which is lower than its fusing-point. Its vapour has a very strong and peculiarly characteristic smell, much resembling that of garlic; its density is 10.37 (GRAHAM). On account of the volatility of arsenic its *fusion* is difficultly accomplished, but may be effected by heating it in a sealed tube, under the pressure of its own vapour. Heated in the air, it easily takes fire, burns with a blue flame, and produces copious white fumes of oxide. Exposed to a moist air, or boiled in water, it gradually becomes incrustated with a gray powder, which is an imperfect oxide, or mixture of metallic arsenic and arsenious acid. Berzelius found that, in three months, 100 parts of the metal acquired an increase of about 8.5. This metal and all its compounds are virulent poisons. Its equivalent number is 38. (37.6 GMELIN, 37.7 BERZELIUS, 38 THOMSON.)

Native arsenic has been found in Saxony, Hanover, France, Bohemia, and Cornwall. It usually occurs in rounded masses, or nodules, of a

foliated lamellar texture, in the veins of primitive rocks, and is often associated with silver, cobalt, lead, and nickel ores.

ARSENIC AND OXYGEN.—There are two definite compounds of arsenic and oxygen, which are both capable of forming combinations with other metallic oxides. They redden litmus and are soluble in water, and have thence been termed *arsenious* and *arsenic acids*.

ARSENIOUS ACID. WHITE ARSENIC. WHITE OXIDE OF ARSENIC. ($Ar + 110$) or AR.—This is the best known, and most commonly occurring compound of arsenic. It may be procured by the combustion of the metal; but as it is evolved during certain metallurgic processes, that mode is rarely resorted to. It is abundantly prepared at Joachimsthal in Bohemia, from arsenical pyrites and arsenical cobalt ores, which are roasted in reverberatory furnaces, and the vapours condensed in a long chimney, the contents of which, submitted to a second sublimation, afford the *white arsenic* of commerce.

Arsenious acid generally occurs in white, semi-transparent, brittle masses, of a vitreous fracture, nearly tasteless, and becoming opaque when long kept, in consequence, apparently, of change in its mechanical texture. The density of the vitreous acid is 3.7385, that of the opaque, or friable, is 3.698, (GUIBOURT,) 3.729, (HERAPATH, *Phil. Mag.*, LXIV. 322.) By slow sublimation, arsenious acid forms brilliant octoëdral and tetraëdral crystals; and Wöhler has found it in six-sided scales, derived from a rhombic prism. (*Ann. de Ch. et Ph.*, LI. 201.) The crystals, as well as the fused or vitreous acid, become opaque, whether exposed or not to air, but exposure accelerates the change. Arsenious acid is volatile at 380° , and *its vapour is inodorous when perfectly free from metallic arsenic*. (PARIS, *Quarterly Journal of Science and Art*, vol. vi.) The density of this vapour is stated by Mitscherlich to be about 13.00. According to Klaproth, 1000 parts of water at 60° , dissolve from $2\frac{1}{2}$ to 3 of white arsenic; and 1000 parts of water at 212° , dissolve rather more than 77 parts, and about 30 parts are retained in permanent solution. According to Guibourt, 100 parts of boiling water dissolve 9.68 parts of the vitreous acid, and 11.47 of the opaque acid, and when the solutions cool to 60° , 1.78 parts of the former and 2.90 of the latter are permanently retained; the first solution reddens litmus, but the second not only does not redden it, but even restores the blue colour. When the powdered vitreous acid is covered with ammonia, a little heat, but no combination, ensues, and the whole of the ammonia may be removed by water, but the washed powder has now acquired the properties of the opaque acid. The aqueous solution of arsenious acid tastes slightly sour and sweet; it furnishes tetraëdral and octoëdral crystals by very slow or spontaneous evaporation, which are anhydrous. 80 parts of alcohol at 60° dissolve 1 part of this acid: it is also soluble in ether and in fixed and volatile oils. The greater number of the acids dissolve it without forming definite combinations. During its crystallization from a somewhat dilute hydrochloric solution, sparks and flashes of light are often perceived (p. 219). Distilled with an equal weight of dry acetate of potassa, an anhydrous compound of the acetic and arsenic acid passes over, of a most nauseous odour, and so attractive of water as to absorb it rapidly from the air, and with the evolution of so

much heat as occasionally to ignite the compound, which burns with a red flame, and exhales arsenious acid. (BERZELIUS.)

Arsenious acid is virulently poisonous, producing a set of peculiar symptoms, ultimately followed by inflammation and gangrene of the stomach and intestines: it also proves fatal when applied to a wound; and as the local injury is not sufficient to cause death, it is probable that an induced affection of the nervous system and of the heart is the immediate cause of the mischief. (BRODIE'S *Observations and Experiments on the Action of Poisons*, *Phil. Trans.*, 1812, p. 209.) To get rid of the poison by producing copious vomiting and purging, and to pursue the usual means for subduing and preventing inflammation, are the principal points of treatment to be adopted in cases where this poison has been taken. (OREILA, *Traité des Poisons*, i. 123. CHRISTISON, *on Poisons*.)

The relative proportions of the components of arsenious acid have been variously stated; but the experiments of Berzelius, corroborated by the results of other analysts, have proved that the oxygen in the arsenious acid is to that in the arsenic acid as 3 to 5; hence, *arsenious acid*, or the *white oxide*, may be considered as composed of

					Thenard.	Davy.	Proust.	Mitscherlich.	Berzelius.
Arsenic	. . . 1	. 38	. 76	. 74.24	. 75	. 75.2	. 75.73	. 75.782	
Oxygen	. . . 1½	. 12	. 24	. 25.76	. 25	. 24.8	. 24.27	. 24.218	
Arsenious acid	1	50	100	100.00	100	100.0	100.00	100.000	

Native White Arsenic occurs in prismatic crystals, and in a pulverulent form: it is found in Saxony and Hungary.

COMBINATIONS OF ARSENIOUS ACID WITH BASES. ARSENITES.—These salts, when heated, either evolve arsenious acid or metallic arsenic: in the latter case they are converted into *arseniates*: heated with charcoal metallic arsenic sublimes. The alkaline arsenites, when in solution, are decomposed by lime and the salts of lime, and a white precipitate of *arsenite of lime* falls: they are precipitated green by solutions of copper, and yellow by nitrate of silver. They are not precipitated by sulphuretted hydrogen, except excess of a stronger acid be present: in this way the hydrochloric solutions of those arsenites which are insoluble in water may also be decomposed. When metallic arsenic is heated with hydrate of potassa, hydrogen gas is evolved and arsenuret of potassium and arsenite of potassa are formed; the potassa therefore and the water are both decomposed; if the heat be raised to redness the arsenious acid is resolved into metallic arsenic and arsenic acid: with hydrate of soda the phenomena are similar; with hydrates of lime and baryta no arsenic acid is produced. (SOUBEIRAN, *Ann. de Ch. et Ph.*, xliii.)

The *arsenites of ammonia*, *potassa*, and *soda*, are easily soluble and uncrystallizable: they are formed by dissolving the acid in the alkaline solutions. Berzelius has shown that the supposed crystals of arsenite of ammonia deposited by the solution of arsenious acid in ammonia, are quite destitute of ammonia, and consist only of arsenious acid. When arsenious acid is dissolved in the alkaline carbonates, it is deposited unaltered by evaporating the solution, so that it is doubtful whether this acid expels carbonic acid, in the humid way. The *arsenites of lime*, *baryta*, *strontia*, and *magnesia*, are difficultly soluble. *Arsenite of potassa* is

the 'active ingredient in the *liquor arsenicalis* of the *Pharmacopæia*, and in *Fowler's mineral solution* or *tasteless ague-drop*. It produces a white precipitate in the protosalts of manganese, a dingy green precipitate in the solutions of iron, a white precipitate in solutions of zinc and tin. Mixed with a solution of sulphate of copper, a precipitate of a fine apple-green colour falls, called, from its discoverer, *Scheele's green*, and is useful as a pigment: it is prepared by dissolving 2 parts of sulphate of copper in 44 of hot water, and gradually adding it to a solution of 2 parts of carbonate of potassa and 1 of arsenious acid in 44 of hot water, the whole being well stirred during mixture: the arsenite of copper in the form of a fine green powder is gradually deposited, and is to be washed and dried at 212° . In the solutions of lead, antimony, and bismuth, arsenite of potassa forms white precipitates: added to nitrate of cobalt, it forms a pink precipitate; and bright yellow, with nitrate of uranium. With nitrate of silver it forms a white precipitate, soon becoming yellow, and very soluble in ammonia. All these precipitates are probably *arsenites* of the respective metals, and, heated by a blowpipe on charcoal, they exhale the smell of arsenic. They are decomposed when boiled in solution of carbonate of potassa or of soda: they are mostly soluble in excess of arsenious acid, and easily soluble in nitric acid, and such other acids as form soluble compounds with their bases.

Native Arsenite of Lead is found in France, in Spain, and in Siberia.

ARSENIC ACID ($ar + 21 O$), or ar' , was discovered by Scheele; it is obtained by distilling a mixture of 2 parts of hydrochloric and 14 of nitric acid off 1 part of arsenious acid; nitric oxide gas is given off, and when the contents of the retort have acquired the consistence of thin syrup, they are poured into a porcelain dish and evaporated by a moderate heat: suddenly, the arsenic acid (which is anhydrous) concretes into an opaque white mass, which should be put, whilst warm, into a well-stopped phial. The hydrochloric acid is only useful in promoting the solution of the white arsenic, which otherwise adheres to the retort and occasions irregular ebullition. Arsenic acid may also be procured by distilling nitric acid off powdered metallic arsenic.

Arsenic acid is a white substance, of a sour taste: it is anhydrous, deliquescent, and uncrystallizable. Its specific gravity is 3.4. It requires for solution 6 parts of cold and 2 of boiling water; its solution reddens vegetable blues, and tastes acid and metallic, and is a virulent poison. When water is poured upon it, a part only is immediately dissolved; and another portion, as is the case with phosphoric acid, remains undissolved; after a time, upon agitating the solution, the whole is taken up. Heated to bright redness, it evolves oxygen, and is converted into arsenious acid. If dry arsenic acid be exposed to air, so as gradually to deliquesce, it sometimes forms crystals which are extremely soluble, and are probably *hydrated acid*. Arsenic acid gives a white precipitate with lime-water, and a peculiar reddish-brown with nitrate of silver. It yields a yellow deposit of a sulphuret of arsenic when its solution is subjected to the action of a current of sulphuretted hydrogen gas.

Arsenic acid consists of

				Proust.	Mitscherlich.	Berzelius.	Thenard.
Arsenic . . .	1	33	65.5	65	65.04	65.283	65.4
Oxygen . . .	$2\frac{1}{2}$	20	34.5	35	34.96	34.717	34.6
Arsenic acid	1	53	100.0	100	100.00	100.000	100.0

ARSENIATES are produced by the union of this acid with the metallic oxides; and many which are insoluble may be formed by adding arseniate of potassa to their respective solutions. They are soluble in dilute nitric acid, and in such other acids as do not form insoluble compounds with their bases, and ammonia precipitates them from these solutions. They are readily decomposed by charcoal at a red heat; but many of them, when heated alone, are unchanged even at a higher temperature. They are decomposed when boiled in solutions of the fixed alkaline carbonates. The soluble arseniates generally give a white precipitate with lime-water: they are not immediately precipitated by solution of sulphuretted hydrogen: protosulphate of iron gives a white precipitate (or yellowish if arsenious acid be at the same time present). With acetate of lead and acetate of zinc they also give white precipitates.

ARSENIATE OF AMMONIA ($A + ar'$) is formed by saturating arsenic acid with ammonia; oblique rhomboidal prisms are obtained on evaporation, which, when gently heated, effloresce and evolve ammonia: at a higher temperature, water is formed, oxide of arsenic sublimes, and nitrogen is evolved, a circumstance first observed by Scheele. According to Mitscherlich (*Ann. de Ch. et Ph.*, xix.), these crystals very closely resemble those of phosphate of ammonia, and consist of

Ammonia . . .	1	17.0	19.2
Arsenic acid . . .	1	58.0	65.5
Water	$1\frac{1}{2}$	13.5	15.3
Arseniate of ammonia	1	88.5	100.0

BINARSENIATE OF AMMONIA is formed by adding to a solution of the above crystals 1 additional proportional of arsenic acid. On evaporation, crystals resembling those of the biphosphate of ammonia are deposited, containing, according to Mitscherlich,

Ammonia	1	17	10.6
Arsenic acid	2	116	72.5
Water	3	27	16.9
Binarsenate of ammonia	1	160	100.0

ARSENIATE OF POTASSA ($P + ar'$), when *neutral*, is deliquescent and uncrystallizable.

BINARSENIATE OF POTASSA ($P + 2 ar'$) may either be formed by adding excess of arsenic acid to potassa, and evaporating, or by heating to redness, in a Florence flask, a mixture of equal parts of nitre and white arsenic; during the latter operation much nitrous gas is evolved, and on dissolving the residue in water, filtering, and evaporating, quadrangular crystals of binarsenate of potassa are obtained, resembling those of the biphosphate of potassa: they are soluble in 5.3 parts of water at 40° , and insoluble in alcohol. Macquer was the first who procured this salt: hence termed *Macquer's neutral arsenical salt*. It is not easily decomposed by

heat alone, and may be fused and kept red-hot without undergoing other change than losing a little acid; but when mixed with about an eighth of charcoal-powder and distilled, metallic arsenic rises, and carbonate of potassa, mixed with part of the charcoal, remains in the body of the retort. This salt, as well as the arsenite, is used for the cure of agues. It is a delicate test of the presence of silver, in solutions of which it occasions a red-brown precipitate: it is also sometimes used to separate iron from manganese; it produces in the persalts of iron a white precipitate, whilst the arseniate of manganese remains in solution. In the crystallized form it consists of

Potassa	1	48	26.4	27.074	} . . 89.91
Arsenic acid	2	116	63.7	65.426	
Water	2	18	9.9	7.500	
Binarseniate of potassa	1	182	100.0	100.000	100.00

ARSENIATE OF SODA ($S + ar'$) is formed by saturating a solution of carbonate of soda with arsenic acid; on evaporation, rhombic prisms are obtained, isomorphous according to Mitscherlich, with phosphate of soda; they effloresce in a dry air, and require, according to Thomson, 10 parts of water at 60° , for solution, and the liquid has alkaline properties. When dropped into solutions of earthy and metallic salts, this salt occasions precipitates in most of them, a table of which is given by Thomson. (*Ann. of Phil.*, xv.) The crystals appear to contain different proportions of water according to the strength of the solution from which they are deposited, and which when concentrated yields them with 8, and when dilute, with 12 equivalents of water, (MARX, *uber das Verhältniss der Mischung zur Form*; Brunswick, 1824:) hence we have them composed of

			Gmelin.			Mitscherlich.
Soda	1	32	19.8	1	32	16.2
Arsenic acid	1	58	35.8	1	58	29.3
Water	8	72	44.4	12	108	54.5
Arseniate of soda	1	162	100.0	1	198	100.0

BINARSENIATE OF SODA. ($S + 2 ar'$).—This salt is formed by adding arsenic acid to a solution of carbonate of soda, till the liquid no longer precipitates chloride of barium: on evaporation and exposure to cold, it yields crystals isomorphous with biphosphate of soda, and composed of

	Anhydrous.			Mitscherlich.	Crystallized.			Mitscherlich.
Soda	1	32	21.6	21.681	1	32	17.4	17.36
Arsenic acid	2	116	78.4	78.319	2	116	63.0	62.70
Water					4	36	19.6	19.94
Binarseniate of soda	1	148	100.0	100.000	1	184	100.0	100.00

The following details respecting the arseniates of soda and potassa are given by Graham (*Elements of Chem.*, 629): to compare them with the preceding statement, it must be remembered that Mr. Graham doubles our equivalent of arsenic, and represents arsenic acid as a compound of 1 atom of arsenic = 76, and 5 of oxygen = 40; his equivalent, therefore, of arsenic acid is 116, and its formula ($ar + 5 o$) or (AsO_5). Dr. Turner, on the other hand, (as in the case of phosphorous and phos-

phoric acid,) uses our equivalent for arsenic, but represents arsenic acid as a compound of 2 atoms of arsenic and 5 of oxygen ($2ar + 5o$), and thus arrives at the same equivalent for arsenic acid as that used by Graham. "When 1 equivalent of arsenic acid is ignited with an excess of carbonate of soda, 3 equivalents of carbonic acid are expelled, and a tribasic arseniate of soda formed, which crystallizes when dissolved in water with 24 equivalents of water, forming the salt $3(so + o) + (ar + 5o) + 24q$, isomorphous with the subphosphate of soda. The same salt is obtained by treating arsenic acid in solution with an excess of caustic soda. When carbonate of soda is added to a hot solution of arsenic acid, so long as there is effervescence, a salt is obtained by evaporation, corresponding with the common phosphate of soda, containing 2 equivalents of soda and 1 equivalent of water, as bases. This salt affects the same two multiples, in its water of crystallization, as phosphate of soda, namely, $24q$ and $14q$, but most frequently assumes the smaller proportion, forming the salt $2(so + o + q) + (ar + 5o) + 14q$. This arseniate is more soluble than the phosphate, and slightly deliquescent in damp air. When to the last salt a quantity of arsenic acid is added, equal to what it already contains, and the solution is highly concentrated, the salt named binarsenate of soda crystallizes at a low temperature. This salt contains 1 equivalent of soda and 2 of water, as bases, and corresponds with the biphosphate of soda: its formula is $(so + o + 2q) + (ar + 5o) + 2q$. The binarsenate of potash, which is analogous in composition, is a highly crystallizable salt: it is sometimes prepared by deflagrating arsenious acid with an equal weight of nitrate of potash. These arseniates of alkalis which contain water as base, all lose that element at a red heat; but, unlike the phosphates, they recover it when again dissolved in water. Arsenic acid, therefore, forms only one, and that a tribasic, class of salts." As regards the comparison of the above arseniates with the phosphates, the reader is referred to the table at page 659.

ARSENATE OF LIME ($C + ar'$) is deposited when arsenic acid is dropped into lime water, or when arseniate of potassa is added to nitrate of lime; it may also be formed by heating a mixture of white arsenic and quick-lime, in which case, as Dr. Wollaston first observed, when it has attained a certain temperature, ignition suddenly ensues, and metallic arsenic sublimes; so that one portion of the arsenious acid confers oxygen upon the other, to convert it into arsenic acid. It is soluble in nitric and hydrochloric acids, and in sulphate, hydrochlorate, and nitrate of ammonia: it also dissolves in arsenic acid. *Hydrated arseniate of lime* (Pharmacolite) occurs native, sometimes in fine capillary crystals. Arseniate of lime consists of

	<i>Artificial.</i>				<i>Laugier.</i>	<i>Native.</i>				<i>Klaproth.</i>
Lime	1	28	32.6		32.5	1	28	24.78		25.00
Arsenic acid . . .	1	58	67.4		67.5	1	58	51.33		50.54
Water					1	3	27	23.89		24.46
Arseniate of lime	1	86	100.0		100.0	1	113	100.00		100.00

ARSENATE OF BARYTA. ($B + ar'$).—When a solution of arseniate of soda is added, not in excess, to a solution of chloride of barium, a

granular precipitate is gradually obtained, which is *neutral* arseniate of baryta; when heated it loses water of crystallization, but is not further decomposed. It consists of

	<i>Anhydrous.</i>			Berzelius.		<i>Crystallized.</i>			Berzelius
Baryta	1	77	57	57.06	1	77	50.3	50.32	
Arsenic acid . . .	1	58	43	42.94	1	58	37.9	37.86	
Water					2	18	11.8	11.82	
Arseniate of baryta	1	135	100	100.00	1	153	100.0	100.00	

SUBSESQUIARSENATE OF BARYTA. ($\frac{1}{2}B + ar'$).—When arsenic acid is dropped into baryta-water, or when the neutral arseniate of baryta is digested in ammonia, a white and difficultly-soluble powder is obtained, composed of

			Berzelius.	Laugier.
Baryta	$1\frac{1}{2}$	115.5	66.6	66.56
Arsenic acid	1	58.0	33.4	33.44
Subsesquiarsenate of baryta	1	173.5	100.0	100.00

BINARSENATE OF BARYTA. ($B + 2 ar'$).—When the neutral arseniate of baryta is dissolved in arsenic acid it yields crystals of the *hydrated binarsenate*: when heated to redness, they leave a compound of

			Mitscherlich.
Baryta	1	77	39.9
Arsenic acid	2	116	60.1
Binarsenate of baryta	1	193	100.0

ARSENATE OF STRONTIA. ($STR + ar'$).—When solutions of nitrate of strontia and arseniate of soda are mixed in atomic proportions, no immediate precipitate appears, but in twenty-four hours small crystals are formed, which are minute rectangular four-sided prisms, tasteless, not affecting vegetable blues, and very sparingly soluble in water. They contain, according to Dr. Thomson,

Strontia	1	52	28.6
Arsenic acid	1	58	31.9
Water	8	72	39.5
Arsenate of strontia	1	182	100.0

ARSENATE OF MAGNESIA ($M + ar'$) is soluble, deliquescent, and uncrystallizable, when there is an excess of acid; but a very difficultly soluble, and *neutral arseniate* may be obtained, partly in powder and partly in tufted crystals, by mixing dilute solutions of sulphate of magnesia and arseniate of soda in atomic proportions, and suffering them to remain at rest for twenty-four hours. The crystals consist, according to Thomson, of 1 atom of anhydrous arseniate of magnesia, and 8 of water; when dried at a temperature of 500° , they lose 6 atoms of water, but still retain 2, which are disengaged at a red heat.

ARSENATE OF MANGANESE. ($MAN + ar'$).—This salt, in a hydrated state, is precipitated in the form of a white powder, when arseniate of potassa is added to chloride of manganese. It is insoluble in water, but dissolves in sulphuric and hydrochloric acids.

PROTARSENATE OF IRON. $(\text{Fe} + ar')$.—Arsenate of ammonia, added to a solution of protosulphate of iron, occasions a precipitate of *protarsenate of iron*. (CHENEVIX, *Phil. Trans.*, 1801.) This salt is at first white, but soon acquires a tint of green; it is sparingly soluble in liquid ammonia, and the solution becomes green in the air. According to Berzelius, the mineral called *Skorodite*, found at Graul, near Schwartzenberg, in small blue-green octoëdral crystals, is a *hydrated protarsenate of iron*.

PERARSENATE OF IRON is an insoluble white powder, which, when heated, loses 17·68 per cent. of water, and becomes red: it is soluble in acids, and soluble, when moist, in caustic ammonia. When the neutral protarsenate of iron is digested in nitric acid and evaporated to dryness, or when the solution is precipitated by ammonia, a *subperarsenate* is obtained.

The *Native Cubic Arseniate of Iron*, analyzed by Vauquelin and by Chenevix, is a compound of the hydrated protarsenate and perarsenate. (BERZELIUS.)

SUBARSENATE OF ZINC is precipitated in a white gelatinous state, when arsenic acid, or an alkaline arseniate, is added to sulphate of zinc. It is insoluble in water, but soluble in arsenic and in nitric acids.

ARSENATE OF TIN.—A white insoluble powder is precipitated by adding arseniate of potassa to protochloride of tin.

ARSENATE OF COPPER is formed by adding an alkaline arseniate to nitrate of copper; it is a blue insoluble powder, and when dried at a temperature not exceeding 212° , appears to be a *hydrated subarsenate*.

The *Native Arseniates of Copper* have been submitted to an elaborate investigation by Chenevix (*Phil. Trans.*, 1801); he has described five varieties, as shown in the following table. (THOMSON, *System*.)

		Acid.		Oxide.		Water.
Variety	1st	1		3·70		2·50
"	2nd	1		2·76		1·0
"	3rd	1		1·72		0·70
"	4th	1		1·80		0·53
"	5th	1		0·88		0·60

ARSENATE OF LEAD. $(\text{Pl} + ar')$.—This salt is formed when arsenic acid is added to nitrate of lead, or when a solution of nitrate of lead is gradually decomposed by the addition of neutral arseniate of soda. It is white, insoluble in water, but soluble in nitric and hydrochloric acids, easily fusible, and consists of

					Berzelius.	Thenard.	Chenevix.
Oxide of lead	1	112	65·9		65·86	64·3	63
Arsenic acid	1	58	34·1		34·14	35·7	37
Arsenate of lead	1	170	100·0		100·00	100·0	100

SUBARSENATE OF LEAD.—When neutral arseniate of soda is added *in excess* to the soluble salts of lead, a white powder falls, composed of

					Berzelius.
Oxide of lead	11½	168	74.3	74.75	
Arsenic acid	1	58	25.7	25.25	
<hr/>					
Subarsenate of lead	1	226	100.0	100.00	

This salt occurs *native* in several of the Cornish mines, and at Beer-alsten, in Devonshire, of a brownish-yellow colour, mamillary, compact, and crystallized in six-sided prisms.

ARSENATE OF ANTIMONY. — Arseniate of potassa throws down a white precipitate in the hydrochloric solution of oxide of antimony.

ARSENATE OF BISMUTH falls in the form of a white powder on adding arsenic acid to nitrate of bismuth; it is insoluble in water, and in nitric acid, but soluble in hydrochloric acid. (THENARD.)

ARSENATE OF COBALT is precipitated of a red colour by the addition of an alkaline arseniate to a soluble salt of cobalt. The cobalt ore, called *peach-blossom* cobalt, is a hydrated diarsenate of cobalt.

ARSENATE OF NICKEL, formed by double decomposition, is an apple-green powder, often granular and crystalline. The mineral called *nickel-ochre* is a *hydrated arseniate of nickel*, composed of 36.20 oxide of nickel, 36.80 arsenic acid, 25.50 water, and a trace of cobalt. (BERTHIER.)

ARSENATE OF URANIUM is thrown down of a straw-colour when arseniate of potassa is added to nitrate of uranium.

CHARACTERS OF THE ARSENITES AND ARSENIATES. — These salts are recognised by the alliaceous odour which they exhale when heated in a tube with a little carbonaceous matter, when they also afford a metallic sublimate. The *arsenites*, when heated alone, generally lose part of their acid, which forms a crystallized sublimate; but the *arseniates*, under the same circumstances, retain their acid, unless partially decomposed, as it sometimes is, by the base. The *arsenites*, when dissolved in dilute hydrochloric acid, and tested by a current, or strong solution of sulphuretted hydrogen, give a yellow cloud of sulphuret of arsenic; but the *arseniates* are not thus decomposed.

ARSENIC AND CHLORINE. CHLORIDE OF ARSENIC. ($ar + 1\frac{1}{2}C$). — This compound may be formed: 1. By throwing finely-powdered arsenic into chlorine; the metal burns and produces a volatile liquid compound: or by passing dry chlorine over arsenic placed in a curved tube or adopter, and gently heated: the resulting vapour of the chloride should be condensed in a receiver cooled by ice, and may be purified by redistilling it off a little powdered arsenic. 2. Distil 6 parts of corrosive sublimate with 1 of powdered arsenic; the chloride passes into the receiver in the form of an unctuous fluid, formerly called *butter of arsenic*. 3. A preferable process for obtaining this compound is that of Dumas. (*Ann. de Ch. et Ph.*, xxxiii. 360.) 1 part of arsenious acid with 10 parts of sulphuric acid, are put into a tubulated retort, and the temperature raised to about 212°. Fragments of fused common salt are then to be thrown in by the tubulature; by continuing the heat, and successively adding the salt,

chloride of arsenic is obtained; it distils over, and may be condensed in cold vessels. Very little hydrochloric acid is disengaged, but towards the end of the operation, a portion of hydrated chloride of arsenic is produced, which floats upon the pure chloride, and appears more viscid and colourless; it may be deprived of water by redistillation with concentrated sulphuric acid. Mixed with a larger quantity of water, the chloride of arsenic is decomposed, and arsenious acid is formed, hydrochloric acid being at the same time produced.

When sulphur or phosphorus are heated in this chloride they are dissolved, but again deposited on cooling. It combines with oil of turpentine and olive-oil. It absorbs about ten times its volume of chloro-carbonic acid, but gives it off again on dilution with water. Chloride of arsenic consists of

					J. Davy.	
Arsenic	1	38	41.3	40		
Chlorine	$1\frac{1}{2}$	54	58.7	60		
<hr/>						
Chloride of arsenic	1	92	100.0	100		

No chloride corresponding with arsenic acid has hitherto been obtained, but when excess of chlorine is passed over arsenic, a white crystalline sublimate sometimes makes its appearance, which is probably a *perchloride*. When a mixture of arsenic and calomel is distilled, a dark-brown sublimate is obtained, which is said to be a mixture of calomel with a *subchloride* of arsenic.

IODIDE OF ARSENIC ($ar + 14l$), obtained by heating 1 part of arsenic with 3 or 4 of iodine, is of a deep-red colour, and volatile, so that it may be purified by sublimation. When acted upon by water, it produces hydriodic and arsenious acids; and on evaporating the solution a sub-iodide? of arsenic is obtained in nacreous crystals, which are resolved by heat into arsenic and iodide of arsenic. (PLISSON, SERULLAS, HOTTOT, *Jour. de Pharm.*, Jan. and March, 1828.)

BROMIDE OF ARSENIC. ($ar + 14b$).—Bromine and arsenic act intensely on each other with the evolution of heat and light, and form a crystallizable compound which fuses at 70° , and boils and evaporates at 430° . By the action of water, it yields arsenious and hydrobromic acids, and on evaporation, crystals of pearly lustre, probably a subbromide. (SERULLAS, *Ann. de Ch. et Ph.*, xxxviii. 318.)

FLUORIDE OF ARSENIC is obtained by distilling a mixture of 5 parts of powdered fluor-spar with 4 of white arsenic and 8 of sulphuric acid. A colourless fuming liquid passes over, which is decomposed by water, and by the contact of glass. Unverdorben, who first examined this compound, states its specific gravity to be 2.73. It is extremely volatile, and fumes in the air. The specific gravity of its vapour exceeds 4. It appears to be a *sesquifluoride*. It combines without decomposition with ammonia. In the above process, silicated fluoric acid is also formed at the expense of the glass retort, but it escapes in the gaseous form, while the fluoride of arsenic may be condensed in a bent tube surrounded by ice.

ARSENIC AND HYDROGEN. ARSENURETTED HYDROGEN GAS.—According to Thenard, this gas is best obtained from a powdered alloy, of 3 parts of tin and 1 of arsenic, mixed with a portion of powdered arsenic, and acted on by hydrochloric acid. It may also be obtained by the action of the following alloy upon water. Mix 2 parts of antimony with 2 of cream of tartar, and 1 of white arsenic, and heat the mixture strongly for 2 hours in a covered crucible. When cold, a button of the triple alloy of potassium, antimony, and arsenic, will be obtained, fragments of which may be transferred under a jar inverted in water. (*Quart. Jour.*, xiii. 225.) This alloy should be carefully excluded from air and moisture. Soubeiran recommends that an alloy should be obtained by fusing arsenic with its weight of zinc, and that the gas should be procured by the action of this alloy on strong hydrochloric acid. When a mixture of white arsenic and granulated zinc is acted on by sulphuric acid diluted with 4 parts of water, a mixture of hydrogen and arsenuretted hydrogen is also obtained. Too much caution cannot be observed to avoid inhaling the smallest portion of this gas, for it is extremely poisonous: Gehlen, the eminent German chemist, fell a sacrifice to its deleterious agency; suspecting that the gas was escaping from some part of the apparatus he was using, he applied his nose for the purpose of detecting it, and although he respired a very small quantity, probably a few hundredths of a grain only, he was seized in about an hour with violent vomiting, shivering, and extreme debility, which proved fatal. (*Ann. de Ch. et Ph.*, iii. 135.)

After standing some time over water, arsenuretted hydrogen deposits a small quantity of brown matter, which appears to be a *hydruret of arsenic*. It is decomposed, and deposits arsenic at high temperatures: exposure to intense cold is said to occasion its liquifaction. It may be kept in dry and well-closed vessels without change. It smells strongly alliaceous; it extinguishes a taper, and burns with a pale-blue flame, forming water, arsenious acid, and hydruret of arsenic, the latter being deposited in the form of a brown crust. It is sparingly absorbed by water and has no effect upon vegetable-blue colours. If detonated with excess of oxygen, arsenious acid and water are formed.

If bubbles of chlorine be passed up into a jar of arsenuretted hydrogen standing over warm water, flame and explosion are often produced, hydrochloric acid is formed, and a brown hydruret is deposited; but if the gas be passed in the same way by successive bubbles into chlorine, no inflammation results, absorption takes place, and hydrochloric acid and chloride of arsenic are formed. If the arsenuretted hydrogen be not very pure, and when the gases are cold, inflammation seldom follows their mixture, but the experiment requires caution, for if a bubble chance to inflame in a mixture of chlorine and arsenuretted hydrogen, the jar would be shattered. Chlorine, added to a mixture of sulphuretted with arsenuretted hydrogen, causes a deposit of sulphuret of arsenic. Nitric acid suddenly decomposes arsenuretted hydrogen; water, oxide of arsenic, nitrous acid, and nitric oxide, are the results. With iodine it yields hydriodic acid and iodide of arsenic. It is decomposed by the action of phosphorus, sulphur, potassium, sodium, and tin, at high temperatures. It is not affected by hydrochloric nor phosphoric acids, nor by solutions of the alkaline sulphurets. Many of the metallic oxides and salts decompose

it. Corrosive sublimate is a most delicate test of its presence; as soon as it comes in contact with it, calomel is formed, and a metallic film of arsenic and mercury. Bubbles of the gas, passed through a solution of corrosive sublimate, are similarly decomposed. It is absorbed and decomposed by a solution of sulphate of copper. It is not altered by alcohol or ether; the fixed oils absorb it slowly, and acquire a thicker consistency. Oil of turpentine absorbs it, and becomes thick, milky, and sour, and deposits crystals, which, when heated, smell of arsenic and turpentine.

According to Dumas and Soubeiran (*Ann. de Ch. et Ph.*, xliii.), the specific gravity of arsenuretted hydrogen is 2.695; it becomes liquid at -40° under ordinary pressure. When the pure gas is decomposed by heat, 1 volume yields $1\frac{1}{2}$ of hydrogen; when detonated with oxygen, each volume requires $1\frac{1}{2}$ volume for its perfect combustion, water and arsenious acid being the results. It is, therefore, probably composed of $1\frac{1}{2}$ equivalent of hydrogen, and 1 of arsenic, or of 1 volume of arsenic vapour and 3 volumes of hydrogen condensed into 2 volumes.

HYDRURET OF ARSENIC is the brown compound deposited in several cases of the imperfect decomposition of arsenuretted hydrogen gas. It is formed when an alloy of 10 parts of arsenic and 1 of potassium is acted upon by water. When in the electrolysis of water, the negative electrode is formed of arsenic, no hydrogen gas is evolved, but it combines with the arsenic to form this hydruret. It is a dark brown substance, inodorous and tasteless, and is not decomposed by a red heat; heated in the air it burns into water and arsenious acid.

ARSENIC AND SULPHUR. PROTOSULPHURET OF ARSENIC. RED SULPHURET OF ARSENIC. REALGAR. (*Ar* + *S*).—By slowly fusing a mixture of metallic arsenic and sulphur, or by heating arsenious acid, charcoal, and sulphur, a *red sulphuret of arsenic* is obtained. It is crystallizable, and of a vitreous fracture: its specific gravity is 3.4. It may be sublimed, unaltered, in close vessels.

It is usually known under the name of *Realgar*, and occurs *native* in Germany and Switzerland, in veins of primitive rocks and among volcanic products. Its primitive form is an acute octoëdron. It is used in the preparation of the pyrotechnical compound, called *White Indian Fire*, which consists of 24 parts of saltpetre, 7 of sulphur, and 2 of realgar, finely powdered and well mixed. It burns with a white flame of great brilliancy.

When realgar is digested in a solution of caustic potassa, a part of its sulphur is removed, and a black or brown powder remains, which, when heated, is resolved into realgar and metallic arsenic, and which is regarded as a *subsulphuret*. Realgar consists of

				Native.	
				Klaproth.	Laugier.
Arsenic	1	38	70.37	69	69.57
Sulphur	1	16	29.63	31	30.43
Protosulphuret of arsenic	1	54	100.00	100	100.00

SESQUISULPHURET OF ARSENIC. YELLOW SULPHURET OF ARSENIC. ORPIMENT. SULPHARSENIOUS ACID. (*Ar* + $1\frac{1}{2}$ *S*).—When realgar is fused

with sulphur, or when sulphuretted hydrogen is passed through a solution of arsenious acid in dilute hydrochloric acid, this sulphuret is formed: in the latter case it is in the form of a yellow powder. It is fusible, and assumes a lamellar or crystalline texture on cooling, and may be sublimed without decomposition in close vessels. Heated in the air, it burns with a pale-blue flame, exhaling white fumes and the odour of sulphurous acid. Its specific gravity is 3.45. It sparingly dissolves in boiling water. It is soluble in caustic alkaline solutions: it is insoluble in acids, but is decomposed by nitric and nitrohydrochloric acids. These sulphurets are readily decomposed by fusion with potassa; sulphuret of potassium and a sublimate of metallic arsenic are the results.

Braconnot has employed an *ammoniacal solution of orpiment* as a dye-stuff (*Ann. de Ch. et Ph.*, xii.); the process he recommends is as follows: 1 part of sulphur, 2 of white arsenic, and 5 of pearlash, are to be fused in a crucible at a heat a little below redness: a yellow mass results, which is to be dissolved in hot water and filtered; the filtered solution, diluted with water, is to be treated with weak sulphuric acid, and will give a fine yellow precipitate, which easily dissolves in ammonia, forming a solution at first yellow, but becoming colourless on adding more ammonia. The wool, silk, cotton, or linen, is to be dipped into this solution, more or less diluted according to the colour required, care being taken that no metallic vessels are used; on taking them out they are at first colourless, but, as the ammonia evaporates, become yellow; they are then to be freely exposed to the air, washed, and dried. This colour is very permanent, but soap impairs it. Orpiment is also the basis of the pigment called *King's Yellow*. The composition of orpiment is

				Berzelius.	Native.	
					Laugier.	Klaproth.
Arsenic	1	. 38 . 61.3	. 61	. 61.86	. 62
Sulphur	1½	. 24 . 38.7	. 39	. 38.14	. 38
Sesquisulphuret of arsenic		1	62	100.0	100.00	100

Native Orpiment (the *auripigmentum* of the ancients) is of a bright lemon or golden colour. It is generally massive and lamellar. It occurs both in primitive and secondary rocks in Suabia, Hungary, China, and South America.

PERSULPHURET OF ARSENIC. SULPHARSENIC ACID. ($ar + {}^{24}s$.)—When sulphuretted hydrogen is passed through a concentrated solution of arsenic acid, a yellow precipitate falls, which resembles orpiment in colour, and, like it, may be sublimed without change, in close vessels; it also is easily fusible and soluble in alkaline solutions, but insoluble in boiling water. The same compound is obtained when sulphuretted hydrogen is passed through a concentrated solution of arseniate of potassa, and the resulting sulpho-salt decomposed by hydrochloric acid. This sulphuret of arsenic consists of

				Berzelius.	
Arsenic	1	. . 38 . . 48.7	. . 48.3	
Sulphur	2½	. . 40 . . 51.3	. . 51.7	
Persulphuret of arsenic		1	78	100.0	100.0

The sulphurets of arsenic are all poisonous, though less virulent than the oxides. (ORFILA.) They combine with sulphur, or are soluble in fused sulphur, in all proportions*.

ARSENIO-SULPHURETS.—Each of the preceding sulphurets of arsenic combines, as a *sulphur-acid*, with the opposed, or electropositive sulphurets, or sulphur-bases, to form a class of *sulphur-salts*, called, by Berzelius, *Arsenio-sulphurets*: hence we have three classes of these salts, namely, the *arsenio-protosulphurets*, the *arsenio-sesquisulphurets*, and the *arsenio-persulphurets*.

1. The *arsenio-protosulphurets* (containing realgar, or protosulphuret of arsenic,) are formed, in the dry way, when sulphur-bases are fused with realgar; or when the arsenio-sesquisulphurets are fused with metallic arsenic: when thus obtained, they are decomposed by water, which causes the separation of a black or brown subsulphuret of arsenic, and the residue is an arsenio-sesquisulphuret. These salts cannot be obtained by the direct action of caustic alkali, or of a hydrosulphuret, upon realgar; for in that case, also, an arsenio-sesquisulphuret and black subsulphuret are formed: but they are produced by boiling orpiment in a somewhat concentrated solution of carbonate of potassa, or of soda, and filtering the solution whilst hot; it becomes turbid as it cools, and a brown flocculent precipitate (like Kermes) falls, which is a neutral compound of the alkaline sulphuret with realgar, that is, an *arsenio-protosulphuret of potassium*, or of *sodium*. These salts are red or brown, and mostly insoluble in water. The acids decompose them, and separate realgar.

2. The *arsenio-sesquisulphurets* (containing orpiment, or sesquisulphuret of arsenic,) can only be obtained in the dry way, and in a solid state, for when their solutions are evaporated to a certain degree of concentration, a brown powder is deposited (which is an arsenio-protosulphuret,) and an arsenio-sesquisulphuret, with excess of base, remains in solution: but the decomposition is not perfect, till the latter salt crystallizes. By dilution with water, and boiling, the precipitate is redissolved, and the arsenio-sesquisulphuret reproduced. When orpiment is digested in weak caustic alkali at common temperatures, a compound, containing twice the quantity of orpiment that exists in the neutral compound, is obtained. The arsenio-sesquisulphurets of the alkaline bases are not decomposed by dry distillation; the others are decomposed at a red heat, orpiment is given off, and the sulphur-base remains.

3. *Arsenio-persulphurets*, (containing the persulphuret of arsenic.) These compounds vary in colour; their taste is hepatic, and extremely nauseous and bitter: decomposed by an acid, they give out a very peculiar hepatic odour; when the base is a sulphuret of the metals of the alkalis or alkaline earths, or of glucium or yttrium, or a few of the other metals, these salts are soluble in water; the others are insoluble.

* According to Berzelius there is a compound of arsenic with a larger relative quantity of sulphur, which is formed when a neutral solution of arsenio-persulphuret of potassium is mixed with alcohol, and filtered; the filtered solution is reduced by distillation to some-

what less than half its bulk, and suffered to cool slowly, when it deposits crystalline scales, which are as fusible as sulphur itself, and which he regards as a definite compound of arsenic, with great excess of sulphur. (*Lehrbuch*, ii. 44.)

These salts are often *basic*, and are then mostly crystallizable, which is rarely the case with the *neutral* compounds: the latter are decomposed by dry distillation, and resolved into arsenio-sesquisulphurets and sulphur; but the basic compounds remain unchanged. They are easily decomposed in the open fire. The concentrated solutions of these salts are only very slowly decomposed by exposure to air; when more dilute, they gradually become turbid, and deposit sulphur and sulphuret of arsenic, whilst the solution contains undecomposed salt, together with arsenites and hyposulphites, which, after complete decomposition, become sulphates*.

SULPHURET OF ARSENIC AND IRON is found native in many parts of Europe. It is of a more silvery colour than iron pyrites, and when heated exhales arsenic. It is called *arsenical pyrites*, or *mispickel*, and is an abundant source of arsenious acid. It appears to be a compound of a bisulphuret of iron with binarsenuret of iron; or,

				Chevreul.	Stromeyer.
Iron	2	56	34.2	34.938	36.04
Arsenic	2	76	46.4	43.418	42.88
Sulphur	2	32	19.4	20.132	21.08
Sulphuret of arsenic and iron	1	164	100.0	98.488	100.00

PHOSPHURET OF ARSENIC is formed by heating the metal, or its oxide, with phosphorus; it is gray and brittle, and requires to be preserved out of the contact of air.

SELENIURET OF ARSENIC is formed by dissolving arsenic in fused selenium: it is a black fusible compound, less volatile than its components, so that excess of either may be driven off by heat. At a red heat it boils and sublimates.

ALLOYS OF ARSENIC. ARSENURETS.—Arsenic unites with most of the metals, forming compounds which are generally brittle and comparatively fusible. With *potassium* it forms a brownish compound, which, when put into water, evolves less hydrogen than pure potassium, in consequence of the formation of hydruret of arsenic. With *sodium*, the alloy is either brown and of an earthy aspect, or gray and metallic, according to the proportions of the metals: water acts upon it as upon the former. (GAY

* Having stated thus much respecting the arsenio-sulphurets, I shall not go into the details of their history, or attempt a description of their manifold varieties; of these the reader may form some notion, by reference to Dr. Turner's abstract of the properties of a few of the leading *arsenio-persulphurets* only, (*Elem. of Chem.*, p. 753,) or he may consult Berzelius or Gmelin for a full account of them. The question as to the state of these compounds when in aqueous solution, is involved in the same difficulties with that respecting the solutions of the sulphurets of the alkaline bases, and admits of similar explanation; as an in-

stance, I transcribe the following table of the composition of the crystallized tri-arsenio-persulphuret of sodium, from L. Gmelin.

	Berzelius
Sulphuret of sodium	3 . 117.9 . 28.69 . 28.47
Tripersulphuret of arsenic }	2 . 155.2 . 33.03 . 33.03
Water	15 . 135.0 . 33.08 . 33.50
	1 408.1 100.00 100.00

Or,

Soda	3 . 93.9 . 23.01
Arsenic acid	2 . 115.2 . 28.23
Sulphuretted hydrogen	8 . 136.0 . 33.32
Water	7 . 63.0 . 15.44
	1 408.1 100.00

LUSSAC and THENARD, *Recherches Physico-Chimiques*, tom. i.) The alloy of arsenic and manganese is not known. Arsenic and iron form compounds which are more brittle, hard, and fusible than iron: when iron only contains 2 or 3 per cent. of arsenic, it becomes very brittle when heated. With the acids these arsenurets evolve arsenuretted hydrogen; they retain their influence upon the magnet till the arsenic forms about 50 per cent. Arsenuret of zinc is obtained by placing some arsenic at the bottom of a crucible, or coated retort, and covering it with its weight of granulated zinc, the temperature is gradually raised till the alloy is fused; it is gray, brittle, and granular in texture; with hydrochloric acid it yields chloride of zinc and arsenuretted hydrogen; it contains 43·7 arsenic and 56·3 zinc. (SOUBEIRAN.) Arsenuret of tin is formed by fusion; it is brilliant, crystalline, and brittle. According to Dumas, the most perfectly crystalline compound is a subarsenuret, containing 4 atoms of tin and 1 of arsenic (86 tin + 14 arsenic). Arsenuret of cobalt is formed by heating arseniate of cobalt with charcoal, or in hydrogen gas; or arsenic and cobalt may be fused together; the resulting compound contains 38·5 arsenic + 61·5 cobalt, or about 1 atom and 2. The native arsenuret of cobalt has already been mentioned as one of the ores of that metal. Arsenuret of nickel is made by heating to bright redness, arseniate of nickel in a crucible lined with charcoal: a fused button is obtained which is gray and brittle, and contains 2 atoms of nickel and 1 of arsenic. (BERTHIER.) *Kupfernickel* is a native arsenuret, containing 1 atom of nickel and 1 of arsenic; there is also a native *binarsenuret of nickel*. When *copper* is heated to redness with excess of arsenic, a gray arsenuret is formed, containing 2 atoms of copper and 1 of arsenic. Arsenuret of *lead* is obtained by heating lead with excess of arsenic or of arsenious acid: in the latter case arseniate and bibasic arsenuret of lead are the results; it is a gray, crystalline, brittle compound, not entirely decomposed by heat; it contains about a sixth of its weight of arsenic, and consists, therefore, of 2 atoms of lead + 1 of arsenic. A very minute quantity of arsenic (less than 1 per cent.) is always contained in common lead shot; it gives the lead the property of spherical granulation, when the fused metal is passed through a sieve and suffered to fall through the air till it solidifies. Arsenuret of *antimony* is brittle, hard, and very fusible. Arsenuret of *bismuth* has not been examined, nor are the alloys of arsenic with uranium, titanium, cerium, or tellurium, known.

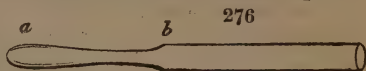
The separation of arsenic from other metals may generally be accomplished by repeated deflagration with nitre, by which it is acidified, and the arseniate of potassa may afterwards be washed out by hot water; but by some of the metals it is very obstinately retained.

TESTS FOR ARSENIC.—As arsenic, either accidentally or intentionally taken, is a very frequent cause of death, and often the subject of judicial inquiry, it becomes of importance to point out the most effectual modes of discovering its presence. Where arsenic proves fatal, it is seldom found in the contents of the stomach after death, but is generally previously voided by vomiting or by stool; and we often can detect it in the matter thrown off the stomach, in the form of a white powder, subsiding in water. The inflammation of the stomach which results is generally a

secondary effect, and takes place equally, whether the poison be swallowed or applied to a wound. If minute quantities of white powder be detected, however, in the stomach after death, or in the matter vomited, it is to be carefully collected, and treated as follows:

(a.) Mix a small portion of it with about two parts of black flux; introduce the mixture into a glass tube, and gradually heat it red-hot in the flame of a spirit-lamp. If arsenic be present, a *steel-coloured sublimate* will attach itself to the cooler part of the tube, which, heated in contact of air, evaporates in fumes *strongly smelling of garlic*.

Berzelius recommends the atom of white arsenic to be introduced into the bottom *a* of a tube, shaped as in the margin, and covered up to *b* with powdered charcoal, previously heated before the blowpipe, to expel all moisture. Heat is then so applied by the flame of a spirit-lamp as to make the charcoal red-hot; the portion *a* is then heated, and the vapour of the white arsenic is decomposed as it passes through the red-hot charcoal, and a metallic film of arsenic deposited in the cold part of the tube. The bottom of the tube is then cut off, and the arsenic recognised as before, by the alliaceous smell of its vapour.



(b.) Boil the suspected matter in a little distilled water; and when the solution has cooled, add a strong solution of sulphuretted hydrogen, or pass the gas through it. If arsenic be present, a *yellow precipitate* will appear. According to Dr. Ure, $\frac{1}{100000}$ of arsenious acid may be detected in water by this test. The hydrosulphuretted alkalis do not affect the arsenious solution unless a drop or two of nitric or hydrochloric acid be added, when the yellow precipitate falls; these tests are, however, equivocal, where very small quantities are to be detected; if a slight excess of alkali be accidentally present, it retains the sulphuret in solution, and excess of acid sometimes occasions a little sulphur to fall.

(c.) To the solution *b* add a drop of solution of carbonate of potassa, and then a drop or two of solution of sulphate of copper. An *apple-green precipitate*, commonly known as *Scheele's Green*, indicates arsenic. The ammonio-sulphate and ammonio-acetate of copper also give the peculiar green precipitate when added to very dilute solutions of white arsenic. This test, however, is fallacious when applied to mixed fluids, for Dr. Christison has shown that the ammoniacal solution of sulphate of copper produces in some vegetable and animal infusions, containing no arsenic, a greenish precipitate, which may be mistaken for Scheele's green; whereas, in other mixed fluids, such as tea and porter, to which arsenic has been added, it occasions none at all if the arsenious acid is small in relative quantity. In some of those liquids a free vegetable acid may be the solvent, but the arsenite of copper is also dissolved by tannin, and perhaps by other vegetable, as well as some animal principles. (TURNER.)

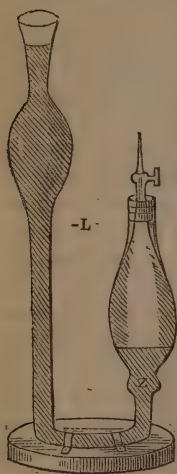
(d.) Add to the solution *b* a drop of nitrate of silver and of solution of ammonia, or of ammonio-nitrate of silver; a *yellow precipitate* indicates arsenic*.

* This is a delicate test of the presence of ammonia. If a drop or two of a solution of arsenious acid and of nitrate of silver be added to pure distilled water | no cloud ensues, but the presence of the smallest trace of ammonia causes a yellow tint.

(e.) The Voltaic pile, made to act by two wires on a little arsenious solution placed upon a piece of glass, develops metallic arsenic at the negative pole; and if this wire be of copper it becomes whitened.

(f.) Mr. Marsh has ingeniously availed himself of the affinity of hydrogen for the detection of arsenic. Whenever hydrogen is generated in contact of any arsenical combination, it combines with the metal which is carried off in the form of arsenuretted hydrogen gas, and the presence of the minutest trace of arsenic in hydrogen may be detected by burning it so that the flame may come into the contact of a plate of glass, or what answers better, of a piece of white earthenware, such as a common plate; it then deposits a dark metallic spot; or if a cold substance be held a little above the flame, arsenious acid condenses upon it; in these cases, the garlic odour of arsenic is perceptible, and if paper has upon it the slightest deposit of white arsenic, it gives a yellow tint when touched with a little diluted ammonio-nitrate of silver. Arsenuretted hydrogen may also be recognised by its blackening effect upon solutions of copper and silver, but sulphuretted hydrogen occasions a similar change. The apparatus for this detection of arsenic is represented in the margin.

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When it is used, the stopcock, which is fitted into the lower bulb by grinding, is removed, and a piece of zinc placed at z; the bulb and tube are then filled to the level L with the liquid to be tested, to which a sufficiency of dilute sulphuric acid is previously added, the stopcock is replaced, hydrogen gas is soon liberated, and filling the lower bulb presses the liquid into the upper one; the gas being now under pressure, may be allowed to issue in a very small jet from the stopcock, and being inflamed may be tested by holding a piece of white earthenware in the flame, and a piece of writing paper an inch or two above it, when the indications of arsenic above mentioned will be observed, provided that metal exists in the tested liquid. The zinc used in these experiments should have been previously examined to ascertain its purity, for it is apt to contain traces of arsenic; it may also contain antimony, or antimony may be present in the tested liquid, in which cases, appearances resembling those of arsenic will ensue, for antimony also goes off with the hydro-

gen; but there is then no garlic odour, no indications of arsenic by the silver test: if the flame from the jet be received into a piece of glass tube the depositions may be more precisely examined, and the metallic film of arsenic may be so heated as to be converted into arsenious acid. In regard to the differences between the stain from arsenic and that from antimony, Mr. Taylor has observed that the former when received on glass is *nut-brown* by transmitted light, while that from antimony is *gray-black*; both are opaque in the centre. Upon the whole, Mr. Marsh's method is certainly a very delicate and efficient means of detecting and discriminating arsenic; if the substances under examination are largely blended with organic matters, these should be got rid of as far as possible by filtration, or by the other usual methods employed in such cases. Minute quantities

of arsenic may sometimes be detected in coloured organic liquids, such as wine, beer, &c., by dipping a piece of paper in them and holding it over a current of sulphuretted hydrogen, or putting it into a bottle filled with that gas; it produces a yellow stain, soluble in ammonia: the only metal by which a similar effect is produced is cadmium, but the sulphuret of cadmium is insoluble in ammonia, and soluble in dilute hydrochloric acid; whereas the sulphuret of arsenic is soluble in ammonia, but insoluble in dilute hydrochloric acid.

§ XXV. MOLYBDENUM.

THE sulphuret is the most common natural compound of this metal: from this ore the *molybdic acid* was first obtained by Scheele in 1778, and from this the metal was obtained by Hielm in 1782. To procure the metal, the native sulphuret is powdered and exposed under a muffle, moderately heated, till converted into a gray powder, which is to be digested in ammonia, and the solution filtered and evaporated to dryness. The residuum is dissolved in nitric acid, re-evaporated to dryness, and violently heated with charcoal. Metallic molybdenum may also be obtained by passing a current of dry hydrogen gas over molybdic acid, strongly heated in a porcelain tube. It should be suffered to cool in the contact of hydrogen.

The metal is of a whitish-gray colour, and of excessively difficult fusion. According to Hielm, its specific gravity is 7.4; according to Bucholz, it is as high as 8.6, and of the colour of silver, somewhat malleable, and unchanged by air. Its specific heat is 0.07218. (REGNAULT.) When exposed to heat and oxygen, molybdenum is acidified, a white crystalline sublimate of *molybdic acid* being formed. At a lower temperature, it first acquires a brown and then a blue film. It is not acted on by dilute sulphuric, hydrochloric, or hydrofluoric acids; boiled in sulphuric acid, sulphurous acid is evolved, and a brown compound formed: it is dissolved by nitric acid, and very readily by nitrohydrochloric acid. It is rapidly oxidized by fusion with saltpetre.

Molybdenum forms three compounds with oxygen, two of which are salifiable, and the third, an acid. Its equivalent number is 48, (47.7 TURNER, 47.96 GRAHAM, 48 GMELIN.)

PROTOXIDE OF MOLYBDENUM. MOLYBDOUS OXIDE. (*mol + o*) is obtained, according to Berzelius, by dissolving molybdic acid, or molybdate of potassa or soda, in hydrochloric acid, and putting a piece of pure zinc into the solution; the liquid changes to blue, red, and black; excess of ammonia is then added, by which protoxide of molybdenum is thrown down in the form of a *black hydrate*, whilst the oxide of zinc is retained in alkaline solution; the hydrate is then washed, and dried in vacuo over sulphuric acid. It is very apt to retain adhering oxide of zinc. Molybdous oxide may be obtained pure by decomposing molybdate of potassa by excess of hydrochloric acid, and agitating the liquid with an amalgam of potassium (containing little potassium); when it has acquired a black colour ammonia is added, which throws down the hydrated oxide. (DUMAS.) In the state of hydrate this oxide is soluble in the acids, but

when anhydrous almost insoluble; it is also insoluble in the caustic and carbonated alkalis, but the recently-precipitated hydrate is soluble in carbonate of ammonia. Molybdous oxide consists of

				Berzelius.
Molybdenum	1	48	85.7	85.69
Oxygen	1	8	14.3	14.31
Protoxide of molybdenum	1	56	100.0	100.00

DEUTOXIDE OF MOLYBDENUM. BINOXIDE OF MOLYBDENUM. MOLYBDIC OXIDE. ($\text{mol} + 2\text{o}$) was obtained by Bucholz, by strongly heating *molybdate of ammonia* rammed down in a crucible: the molybdic acid is reduced by the hydrogen of the ammonia, and a crystalline copper-coloured substance is obtained, of the specific gravity 5.6. It may also be procured, according to Berzelius, by heating a mixture of sal-ammoniac and molybdate of soda in a platinum crucible till the fumes cease: the residue is well-washed, digested in caustic potassa to separate any molybdic acid, and again washed with boiling water. The oxide remains in the form of a black powder, becoming dark-brown when dry, and purple when exposed to the sun's rays.

Dumas observes that although zinc reduces molybdic acid to the state of protoxide, copper only brings it down to deutoxide; if therefore copper, molybdic acid, and hydrochloric acid, are put together, the molybdic acid disappears, and the liquid acquires a deep red tint: it contains the chlorides of copper and molybdenum; by excess of ammonia, the deutoxide of molybdenum is thrown down, and the oxide of copper retained in solution; the precipitate is cleansed by washing with solution of ammonia.

Hydrated molybdic oxide is brown, but becomes green by exposure; it is slightly soluble in distilled water, but insoluble in saline solutions; it is said to redden litmus, but has no other acid characters, and is insoluble in caustic alkalis, but soluble in the carbonates and bicarbonates. When dried in vacuo it becomes dark brown, and loses its solubility, resembling then the anhydrous oxide obtained as above. Molybdc oxide consists of

				Bucholz.	Berzelius.
Molybdenum	1	48	75	73	75
Oxygen	2	16	25	27	25
Deutoxide of molybdenum	1	64	100	100	100

MOLYBDOUS ACID.—When metallic molybdenum and molybdic acid are boiled together in water, a blue solution is formed, which has sometimes been termed *molybdous acid*, and regarded as a distinct stage of oxidizement, but which appears to be a compound of molybdic acid with the deutoxide, and consequently a *molybdate of oxide of molybdenum*. When a current of hydrogen gas is passed over molybdic acid at a red heat, it acquires a blue colour, and becomes converted into molybdous acid. This compound is soluble in water, and yields a rich blue solution, which becomes quite colourless on moderate dilution; it is insoluble in solution of sal-ammoniac; it is immediately converted into molybdic acid by nitric acid, nitrohydrochloric acid, and chlorine; and on the other hand, deoxidizing agents, such as protochloride of tin, or tin-filings and hydrochloric acid, convert molybdic acid into this blue compound. According to Berzelius, the molybdous acid is constituted of 2 atoms of molybdic acid + 1 of molybdic oxide.

PEROXIDE OF MOLYBDENUM. MOLYBDIC ACID. ($mol + 3o$) or mol' .—To obtain this acid, the native sulphuret of molybdenum should be roasted and triturated, to reduce it to powder, and distilled, with 3 or 4 parts of nitric acid, to dryness. This operation should be repeated, till it is converted into an uniform white mass, which consists of molybdic, nitric, and sulphuric acids; the two latter may be expelled by a red heat in a platinum crucible, and the remaining molybdic acid repeatedly washed with boiling-water, in which it is little soluble, will be nearly pure. It may be rendered perfectly pure by solution in ammonia, precipitation by nitric acid, and exposure to heat. Molybdic acid may also be procured by roasting the powdered native sulphuret at a low red-heat, till it ceases to give out sulphurous acid; the residue, by digestion in ammonia, affords a *molybdate of ammonia*, which may be purified by crystallization, and decomposed by a moderate heat in a platinum crucible, so as to leave the molybdic acid.

The molybdic acid, thus procured, is a white powder, of the specific gravity of 3.46, and requiring, according to Hatchett, 960 parts of boiling water for its solution, which is yellow, reddens litmus, but has no sour taste. Its solubility probably differs with its aggregation, for Bucholz found it soluble in about 500 parts of cold water, and others in 570 and 600. Heated to redness in an open vessel, it slowly sublimes, and condenses in brilliant yellowish scales. It dissolves in hot sulphuric acid, forming a solution, which is colourless while hot, but on cooling acquires a blue colour, which is heightened by the addition of soda. Its hydrochloric solution is pale yellowish-green, but becomes blue when saturated by potassa. (HATCHETT, *Phil. Trans.*, 1796.)

It dissolves in the alkalis, forming solutions which are colourless, and from which the molybdic acid is at first precipitated, but afterwards dissolved, by the stronger acids. Molybdic acid is composed of

					Berzelius.	Bucholz.
Molybdenum.	1	.	.	48	.	66.7
Oxygen	3	.	.	24	.	33.3
						33.387
Molybdic acid	1			72		100.0
						100.000
						100.0

MOLYBDATE OF AMMONIA. ($mol' + A.$)—This salt is obtained by dissolving molybdic acid in excess of ammonia, and leaving it to spontaneous crystallization; it forms square prisms, of a pungent metallic taste. When the ammoniacal solution is boiled down, it affords, on cooling, a crystalline mass of *bimolybdate* of ammonia; which, by spontaneous evaporation, may be obtained in rhombic crystals of a pale bluish-green colour, and difficultly soluble in water. Distilled in close vessels this salt yields water, ammonia, and nitrogen, and leaves brown deutoxide; in open vessels the residue is molybdic acid. (BERZELIUS.)

MOLYBDATE OF POTASSA ($mol' + P$) is formed by digesting the acid in potassa; or by heating to redness 2 parts of nitre with 1 of molybdic acid, and lixiviating the mass. Its solution, which is colourless, yields small rhomboidal crystals by evaporation, and affords a precipitate of molybdic acid, to hydrochloric, nitric, and sulphuric acids. When chlorine is passed through it, a white powder falls, difficult of solution in cold

water, but instantly dissolved by hot, which Berzelius suspects to be a *bimolybdate of potassa*.

MOLYBDATE OF SODA ($mol' + S$) is more soluble than molybdate of potassa, and furnishes permanent and transparent crystals. In obtaining this salt, a deposit of a yellowish powder ensues, which is probably a *bimolybdate of soda*.

MOLYBDATE OF LIME ($mol' + C$) is thrown down in the form of an insoluble powder, when alkaline molybdates are added to solutions of lime.

MOLYBDATE OF BARYTA ($mol' + B$) falls in the form of a flocculent precipitate, which collects into crystalline grains, when molybdate of ammonia is added to a solution of nitrate of baryta: by heat it acquires a blue tint. It dissolves in nitric and hydrochloric acids, and these solutions deposit it, when evaporated, in the form of a crystallized rind.

MOLYBDATE OF STRONTIA ($mol' + Str$) is insoluble in water.

MOLYBDATE OF MAGNESIA ($mol' + M$) is soluble in water, and forms clusters of small prismatic crystals, which become yellow when heated, and lose 28 per cent. of water: it dissolves in 12 to 15 times its weight of water. (BERZELIUS.)

MOLYBDATE OF MANGANESE ($mol' + Man$) is a brownish-white and somewhat soluble powder. (RICHTER.)

MOLYBDATE OF PROTOXIDE OF IRON is insoluble, and of a dark-brown colour. (SCHEELÉ.)

MOLYBDATE OF PEROXIDE OF IRON is a yellowish-brown precipitate, decomposed by caustic alkali.

MOLYBDATE OF ZINC is insoluble in water, white, pulverulent, and soluble in the stronger acids: It is obtained by mixing the solutions of molybdate of ammonia and sulphate of zinc. (BRANDES.)

MOLYBDATE OF PEROXIDE OF TIN is a gray powder, insoluble in water, soluble in caustic potassa and in hydrochloric acid, but not altered by nitric acid.

MOLYBDATE OF CADMIUM.—When solutions of molybdate of ammonia and sulphate of cadmium are mixed, a grayish-white powder is thrown down, which when gently ignited becomes brown. (BRANDES.)

MOLYBDATE OF COBALT is precipitated of a dirty-yellow colour, but becomes red by drying: it is decomposed by the alkalis and by the stronger acids. (BERZELIUS.)

MOLYBDATE OF NICKEL is a pale-green powder, soluble in boiling water. When molybdic acid is added to nitrate of nickel, a white precipitate falls, provided there is no excess of nitric acid. (HATCHETT.)

MOLYBDATE OF LEAD. ($mol' + Pl.$)—This compound is precipitated in the form of an insoluble powder, on mixing solutions of molybdate of

ammonia and nitrate of lead; it is of a pale-yellow colour, soluble in nitric acid and in caustic alkalis. It occurs *native*, crystallized, and of different shades of yellow; it was first discovered in Carinthia, and has since been found in Mexico, Hungary, and Saxony; its density is 5·7; it was analyzed by Hatchett. (*Phil. Trans.*, 1796, p. 323.)

It consists of

				Native.		Artificial.
				Hatchett.	Göbel.	Berzelius.
Oxide of lead	1	112	60·87	60·4	59·5	64·42
Molybdic acid	1	72	39·13	39·6	40·5	35·58
Molybdate of lead	1	184	100·00	100·0	100·0	100·00

MOLYBDATE OF COPPER is yellow-green, difficultly soluble in water, and easily decomposed by acids and alkalis. (BERZELIUS.)

MOLYBDATE OF URANIUM is a pale-yellow powder, soluble in the stronger acids and in carbonate of ammonia; when heated it becomes blue: it is obtained by adding molybdate of ammonia to persulphate of uranium: it consists of 43·75 molybdic acid + 56·25 peroxide of uranium. (BRANDES.)

CHLORIDES OF MOLYBDENUM.—According to Berzelius there are three *chlorides of molybdenum*, corresponding in composition to the oxides.

PROTOCHLORIDE OF MOLYBDENUM ($mol + c$) is obtained by dissolving the protoxide, to saturation, in hydrochloric acid; the solution is of a very deep red-brown colour, and leaves on evaporation a viscid mass, soluble in water. It forms double salts with sal-ammoniac, and with chloride of potassium.

BICHLORIDE OF MOLYBDENUM. ($mol + 2c$).—This compound is formed by heating metallic molybdenum in pure and dry chlorine; the metal burns, and a very dark-red vapour fills the retort, which condenses into crystals much resembling iodine; they are fusible, volatile, and in the air first fume a little; and then deliquesce into a black liquid, which changes colour in proportion to the water it absorbs, becoming blue-green, green-yellow, dark-red, rose-coloured, and lastly, yellow. When the crystals are thrown into water, much heat is evolved; if the solution be dilute, it becomes green or blue in consequence of oxidizement. This chloride forms a double *ammonio-chloride of molybdenum* with sal-ammoniac, but does not combine with the chlorides of potassium or sodium.

PERCHLORIDE OF MOLYBDENUM ($mol + 3c$) is formed when molybdic acid is dissolved in hydrochloric acid: it is obtained in the solid form, when a current of chlorine is passed over gently-heated deutoxide of molybdenum; a white or yellowish crystalline sublimate is formed, and molybdic acid remains in the tube: this compound is less volatile than the bichloride, but it rises in vapour at a temperature below redness: it does not fuse. It readily dissolves in water, and is soluble in alcohol: its taste is sharp, astringent, and afterwards sour. (BERZELIUS.) According to H. Rose (*Ann. de Ch. et Ph.*, LXVI. 218), the compound resulting from the above process contains 2 atoms of molybdic acid + 1 atom of perchloride of molybdenum, its ultimate elements being ($3mol + 6o + 3c$); it is therefore an *oxichloride of molybdenum*.

IODIDES OF MOLYBDENUM.—Iodine has no action on metallic molybdenum at any temperature. *Protiodide of Molybdenum* ($mol+i$) may be formed by dissolving the protoxide in hydriodic acid. *Biniodide of Molybdenum* ($mol+2i$) is produced when the deutoxide is dissolved in hydriodic acid; the solution yields dark-red crystals on evaporation.

BROMIDE OF MOLYBDENUM has not been examined.

PROTOFLUORIDE OF MOLYBDENUM ($mol+f$) is formed by dissolving the hydrated protoxide in hydrofluoric acid; a dark-purple solution is obtained, which by very careful evaporation leaves a purple viscid residue; at a higher temperature it becomes brown, and loses its perfect solubility in water: it forms triple compounds with ammonia, and with the fluorides of potassium and sodium.

BIFLUORIDE OF MOLYBDENUM ($mol+2f$) is obtained by saturating hydrofluoric acid with the deutoxide: on evaporation a black crystalline compound is obtained, which yields a red aqueous solution: it forms double salts with ammonia, potassium, and sodium.

PERFLUORIDE OF MOLYBDENUM ($mol+3f$) is the result of the solution of molybdic acid in hydrofluoric acid; it yields, on evaporation, a yellow uncrystallizable residue, which easily acquires a blue tinge from dust, or other reducing agents.

MOLYBDENUM AND SULPHUR.—There are three *sulphurets of molybdenum*, two of which correspond with the deutoxide and with molybdic acid, and the third contains 4 equivalents of sulphur; no *protosulphuret*, corresponding with the protoxide, has as yet been formed.

BISULPHURET OF MOLYBDENUM ($mol+2s$) is produced artificially by intensely heating a mixture of molybdic acid and sulphur, out of the contact of air. It forms the *native sulphuret*, and consists of

				Bucholz.	Brandes.
Molybdenum	1 . .	48 . .	60 . .	60 . .	59.6
Sulphur	2 . .	32 . .	40 . .	40 . .	40.4
Bisulphuret of molybdenum	1	80	100	100	100.0

Native Sulphuret of Molybdenum is found in Bohemia, Sweden, and near Mont Blanc, disseminated in a gray granite. It has been found in England, chiefly in Cornwall; and in Scotland, in Inverness-shire. It rarely occurs crystallized; generally massive, and in easily-separable laminae. It is soft and unctuous to the touch, and in colour much like lead; infusible, and unchanged by heat when air is excluded. Its properties have already been referred to, as a source of molybdenum. It is found exclusively in primitive rocks; generally in granite, and with quartz.

TERSULPHURET OF MOLYBDENUM ($mol+3s$) is obtained by saturating a strong solution of a molybdic salt with sulphuretted hydrogen, and then adding hydrochloric acid; a dark-brown precipitate falls, which becomes black on drying, and which, when heated in close vessels, gives off sulphur, and becomes bisulphuret: it dissolves slowly in the caustic alkalis, and more easily in the alkaline hydrosulphurets.

It consists of

Molybdenum	1	48	50	Berzelius.
Sulphur	3	48	50	49·72
				50·28
Tersulphuret of molybdenum	1	96	100	100·00

This sulphuret combines with the sulphurets of the electropositive metals (alkaline bases), and forms a class of *sulphur-salts*, which may be called *molybdo-tersulphurets*.

MOLYBDO-TERSULPHURET OF POTASSIUM. $(mol + 3s) + (po + s)$.—

This salt is formed by saturating molybdate of potassa by sulphuretted hydrogen, and evaporating; it forms prismatic crystals of a beautiful green and iridescent lustre: by transmitted light they are ruby red, soluble in water, and insoluble in alcohol; on the addition of the stronger acids, sulphuretted hydrogen is evolved, tersulphuret of molybdenum is precipitated, and a salt of potassa remains in solution. This salt is anhydrous, and consists of

Sulphuret of potassium	1	56	36·8	Berzelius.
Tersulphuret of molybdenum	1	96	63·2	35·57
				64·43
Molybdo-tersulphuret of potassium	1	152	100·0	100·00

Similar soluble *molybdo-tersulphurets* may be formed with sulphurets of sodium and lithium, and with those of barium, strontium, and calcium; and several insoluble *molybdo-tersulphurets* are obtained by double decomposition.

PERSULPHURET OF MOLYBDENUM. QUADROSULPHURET OF MOLYBDENUM. $(mol + 4s)$.—This compound is obtained as follows: saturate bimolybdate of potassa with sulphuretted hydrogen, and boil the resulting turbid solution for some hours in a retort; when it cools, a black light powder, and red crystalline scales are deposited, which must be separated as far as possible; the red crystalline deposit is then washed upon a filter with water, till the washings no longer afford a *red* (not a brown) precipitate with hydrochloric acid; the residue upon the filter is then treated by boiling water, and the dark-red solution which filters through is decomposed by excess of hydrochloric acid; a bulky dark-red or brown precipitate falls, which is the quadrosulphuret; it is washed and dried, during which it shrinks, acquiring a gray lustre, and giving a cinnamon-brown powder. It consists of

Molybdenum	1	48	42·86	Berzelius.
Sulphur	4	64	57·14	42·58
				57·42
Persulphuret of molybdenum	1	112	100·00	100·00

This, like the tersulphuret, combines with the protosulphurets of the electropositive metals, and forms *molybdo-persulphurets*; they are rarely crystallizable, and of a red or orange colour.

SALTS OF THE OXIDES OF MOLYBDENUM.—There are three classes of these salts: those of the *protoxide*; of the *deutoxide*; and of *molybdic acid*.

1. The salts of the *protoxide* are black or deep purple; they have a purely astringent taste. 2. The salts of the *deutoxide*, when anhydrous, are nearly black, but red when they contain water of crystallization: their solutions have an astringent, sourish, and metallic taste; they are rendered brown by infusion of galls, and a gray-brown precipitate falls; ferrocyanuret of potassium occasions a dark-brown precipitate, which is insoluble in excess of the precipitant. They are rendered black by an immersed plate of zinc, and a black zinciferous protoxide of molybdenum falls. 3. The *molybdic acid*, before it has been heated, is soluble in the other acids, and produces a class of compounds which, in some of their characters, resemble the common salts; but they combine with the alkalis in the manner of a double acid.

There is also a class of molybdic compounds of a deep-blue colour; they are double salts, the basis of which is a compound of the deutoxide with molybdic acid; the *sulphate* thus formed is of a deep-blue colour, but becomes quite colourless when diluted with 3 or 4 parts of water.

Before the blowpipe molybdic acid melts by itself upon the charcoal with ebullition, and is absorbed. In a platinum spoon it emits white fumes, and is reduced in the interior flame to molybdic acid, which is blue, but in the exterior flame it is again oxidated and becomes white. With microcosmic salt, in the exterior flame, a small proportion of the acid gives a green glass, which by gradual additions of the acid passes through yellow-green to reddish, brownish, and hyacinth-brown, with a slight tinge of green. In the interior flame the colour passes from yellow-green, through yellow-brown, and brown-red, to black; and if the proportion of acid be large, it acquires a metallic lustre, like the sulphuret, which sometimes remains after the glass has cooled. Molybdic acid is but sparingly dissolved by borax. In the exterior flame the glass acquires a gray-yellow colour. In the interior flame black particles are precipitated from the clear glass, leaving it almost colourless when the quantity of molybdenum is small, and blackish when the proportion is large. If, to a glass formed of this acid and microcosmic salt, a little borax be added, and the mixture fused in the exterior flame, the colour becomes instantly reddish-brown: in the interior flame the black particles are also separated, but in smaller quantity. By long-continued heat the colour of the glass is diminished, and it appears yellower by the light of a lamp than by day-light. This acid is not reduced by soda in the interior flame.

§ XXVI. CHROMIUM.

CHROMIUM was discovered by Vauquelin in 1797. It was named from *χρῶμα*, colour, on account of its tendency to produce coloured compounds. Its two native combinations are the *chromate of lead*, in which the metal was originally discovered (*Ann. de Ch.*, xxv. and lxx.), and the *chromite of iron*, which is a compound of the oxides of chromium and iron, found abundantly at Unst in Shetland, and in several parts of Europe and America. Metallic chromium may be obtained by intensely igniting its oxide with about a tenth of its weight of charcoal, but the

reduction is difficult and imperfect. According to Dumas the colour of chrome resembles that of platinum; it scratches glass, and takes a good polish; he could not succeed in fusing it into a button, but only obtained it in a spongy mass superficially fused, though the furnace which he employed was adequate to the fusion of a pound of soft iron in fifteen minutes. When pure it is not magnetic. Its density is 5.9. Heated in the air it becomes superficially protoxidized: it is scarcely attacked by any of the acids, even at a boiling heat: it is, on the other hand, oxidized by the action of alkalis in the presence of oxygen: the carbonates, nitrates, and chlorates, may be used for the purpose. The equivalent of chromium may be assumed as 28.

CHROMIUM AND OXYGEN.—There are two well-defined oxides of chromium: the *protoxide*, which is a salifiable base; and the *peroxide*, or *chromic acid*. According to Berzelius, there also exists a definite *deutoxide*.

PROTOXIDE OF CHROMIUM. SESQUIOXIDE OF CHROMIUM. ($chr + \frac{1}{2}O$) or CHR.—There are several modes of obtaining this oxide:—1. When metallic chromium is exposed to the action of heat and air, it combines superficially with oxygen, and this oxide is formed. 2. The simplest method of obtaining it consists in heating *chromate of mercury* red-hot; mercury and oxygen are given off, and if a pure chromate of mercury is used, the resulting oxide of chrome is of a pure green. 3. It may be obtained by calcining a mixture of equal parts of *chromate of potassa* and sulphur in a close earthen crucible, at a red heat, and washing the green mass which is produced, to dissolve out the sulphate and sulphuret of potassium; the oxide of chromium remains, and is rendered pure by repeated washings. (*Ann. de Ch. et Ph.*, xiv. 299.) 4. By digesting chromate of lead in a mixture of hydrochloric acid and alcohol; an ether is formed, chloride of lead thrown down, and chloride of chromium remains in solution; it may be precipitated in the state of *carbonate of chromium* by carbonate of potassa, and this precipitate washed, and heated red hot, yields the pure protoxide. 5. Chromate of potassa may be dissolved in excess of hydrochloric acid, and sulphuretted hydrogen passed through the solution, which reduces the chromic acid to oxide, the hydrochloric solution of which may be decomposed as above. 6. Chromate of potassa may be boiled with hydrochloric acid and alcohol, by which, as in the case of chromate of lead, a solution of protochloride of chromium is obtained: it may be thrown down either by ammonia or by an alkaline carbonate, and the resulting hydrate or carbonate of chromium may be reduced to the state of pure oxide by calcination. 7. When chromate of lead is heated in a crucible coated with charcoal, oxide of chromium and metallic lead are obtained; they may be separated by triturating the mass and sifting it, when the lead remains upon the sieve. 8. A mixture of equal parts of chromate of potassa and sal-ammoniac, when calcined, yields a green mass, which, when well washed, leaves oxide of chromium. 9. When the vapour of chlorochromic acid is passed through a white-hot tube, chlorine and oxygen are disengaged, and the tube becomes lined with crystals of oxide of chromium, which are of so deep a green as to appear nearly black; their lustre is metallic, and they are so hard as to

scratch glass; their density is 5.21. Berzelius states, that when oxide of chromium, obtained by gently drying the hydrate, is heated nearly red hot in a crucible, it suddenly becomes ignited throughout, without either gaining or losing weight: this occurs in close as well as in open vessels; when cool it has a fine green colour, and has become insoluble in the acids. To render it again soluble, it must be digested in concentrated sulphuric acid, or fused with caustic potassa, or with nitre. In this respect it resembles zirconia and titanica acid.

Protoxide of chromium is of a green colour, the shades of which are deeper in proportion to the temperature to which it has been exposed, infusible and unchanged by heat. After exposure to a red heat it is scarcely attacked by the acids, but readily dissolves in them when recently precipitated, and in the state of hydrate. It is converted into *chromic acid* by deflagration with nitre. Fused with vitrifiable substances, and especially with borax, it confers upon them a characteristic green colour: hence its use in porcelain and enamel painting.

Hydrated Oxide of Chromium.—When this oxide is precipitated from its acid solutions, by the caustic fixed alkalis, it falls in the form of a bulky green powder, slightly soluble in excess of the alkali, but again thrown down on boiling the solution: in this state it is a *hydrate*. It is very sparingly dissolved by excess of ammonia. It may be best obtained by adding a mixture of equal parts of hydrochloric acid and alcohol, in small portions, to a boiling solution of chromate of potassa, until the liquid acquires a pure green colour. When cold, excess of ammonia is added, which precipitates the oxide, combined with a large relative proportion of water; and in this state it readily dissolves in the acids. (THOMSON.)

When tartaric acid is added to the aqueous solution of *chromate of potassa*, it causes an effervescence, and the solution becomes green in consequence of the conversion of the chromic acid into protoxide of chromium: the addition of ammonia now throws down a bulky green tasteless powder, readily soluble in acids, which is also an hydrated oxide of chromium; when heated, it loses as much as thirteen-fifteenths of its weight of water, leaving two-fifteenths of dry protoxide, of a green colour, but difficultly soluble. According to Thomson, this therefore contains a larger quantity of water than any other metallic hydrate. Protoxide of chromium consists of

				Berzelius.
Chromium	1	28	70	70.11
Oxygen	$1\frac{1}{2}$	12	30	29.89
Protoxide of chromium	1	40	100	100.00

Native Protoxide of Chromium has been found in France, in the department of the Rhone, in the form of a green incrustation. It is the colouring-matter of the emerald, and exists in a few other minerals, such as diallage and some varieties of serpentine.

The native oxide is insoluble in the acids, and occurs combined or mixed with silica and alumina, the richest specimens containing not more than 13 per cent.: their shades of green vary accordingly.

DEUTOXIDE OF CHROMIUM.—When nitrate of chromium is decom-

posed at a dull red-heat, an insoluble *brown deutoxide* is formed. When heated with hydrochloric acid, chlorine is evolved, and a protochloride formed. According to Berzelius, when a solution of chromic acid in sulphuric acid is digested with the hydrated protoxide of chromium, a brown solution is obtained, from which the deutoxide, in the state of hydrate, is precipitated by the caustic alkalis: he says that it dissolves in, and gives distinct salts with the acids; distinguished from the protosalts by their brown colour, and convertible into protosalts by deoxidizing agents. At a bright red-heat this deutoxide loses oxygen, and becomes protoxide, so that it is difficult to obtain it pure, for if the protonitrate be not adequately heated, the product contains nitric acid, and if over-heated, protoxide of chromium. According to Döbereiner, this oxide may be regarded as a *dichromate of chromium*; or a compound of 2 atoms of the green oxide and 1 of chromic acid: Mauss also regards it as a chromate of the protoxide.

CHROMIC ACID. PEROXIDE OF CHROMIUM. ($chr + 3o$) or chr' .—Pure chromic acid may be procured, according to Unverdorben, by the following process, from the *native chromite of iron*. Reduce it to a fine powder, and expose it to a bright red-heat for two hours, mixed with half its weight of nitre; wash the contents of the crucible, and add to the lixivium nitric acid sufficient to neutralize the excess of potassa; in this way a solution of nitrate and of chromate of potassa is obtained. Upon adding nitrate of lead to this solution, *chromate of lead* is precipitated in the form of a yellow powder, which is to be washed, dried, and heated to redness. Of this chromate, 4 parts are then well mixed with 3 of finely-powdered and pure fluor-spar (previously heated red-hot), and 5 of concentrated sulphuric acid; this mixture is introduced into a distillatory apparatus of lead or platinum, and gently heated; a red vapour is liberated, which is conducted into distilled water contained in a vessel of platinum: it is thus condensed into a dark orange-coloured liquid; the red vapour is a *fluoride of chromium*, and is resolved by water into hydrofluoric and chromic acids, the solution of which, evaporated in a platinum vessel, leaves pure chromic acid. If, instead of conducting the vapour into water, it be received into a platinum vessel, containing pieces of moist blotting-paper, it is decomposed as before; but the chromic acid is deposited in beautiful acicular crystals, which soon deliquesce.

“Another method of preparing chromic acid has been suggested by M. Arnold Mauss, which consists in decomposing a hot concentrated solution of bichromate of potassa by silicated hydrofluoric acid: the chromic acid, after being separated from the sparingly-soluble fluoride of silicium and potassium, is evaporated to dryness in a platinum capsule, and then redissolved in the smallest possible quantity of water: by this means the last portions of the double salt are rendered insoluble, and the pure chromic acid may be separated by decantation. The acid must not be filtered in this concentrated state, as it then corrodes paper like sulphuric acid, and is converted into chromate of the green oxide of chromium. When it is wished to prepare a large quantity of chromic acid by this process, porcelain vessels may be safely employed in the first part of the operation, provided care is taken to add a quantity of silicated

hydrofluoric acid, not quite sufficient for precipitating the whole of the potassa." (TURNER'S *Elements*.)

Chromic acid was formerly obtained by decomposing chromate of lead, or chromate of baryta, by sulphuric acid; but in that case, when the solution is evaporated, the crystals which are obtained always retain sulphuric acid, and if it be attempted to expel this by heat, part of the chromic acid is itself decomposed. (GAY LUSSAC, *Ann. de Ch. et Ph.*, xvi. 102.)

Chromic acid is of a dark-red colour, becoming almost black when heated; its taste is sour and metallic; it tinges the cuticle yellow; it may be obtained from its aqueous solutions in deliquescent but anhydrous prismatic crystals, of a ruby colour. When heated red-hot, it gives out a portion of oxygen, and becomes the green protoxide; it is energetically acted on and converted into oxide by ammonia. It dissolves in alcohol, and the solution gradually deposits green oxide. It combines with sulphuric acid, and the compound forms octoëdral crystals, formerly mistaken for pure chromic acid. With hydrochloric acid it forms a compound which dissolves gold. It is a powerful bleaching agent. The aqueous solution of chromic acid is decomposed by the sun's rays, and deposits the oxide. Chromic acid appears to be the colouring matter of the ruby. In combination with oxide of tin it forms a pink colour used in porcelain painting. (*Ann. de Ch. et Ph.*, lxi. 433.) The salts of chromic acid are said to be isomorphous with those of the sulphuric and selenic acids. This acid is composed of

				Berzelius.
Chromium	1	28	53.85	53.98
Oxygen	3	24	46.15	46.02
Chromic acid	1	52	100.00	100.00

CHROMATE OF AMMONIA ($chr' + A$) is formed by saturating ammonia with chromic acid, and concentrating the solution over sulphuric acid in vacuo; it forms yellow crystalline scales, having an alkaline reaction, very soluble, and anhydrous. (THOMSON.)

BICHRIMATE OF AMMONIA ($2chr' + A$) is produced when the solution of the preceding salt is concentrated on a sand-heat; it forms crystalline plates, resulting from an oblique rhombic prism (BROOKE, *Ann. of Phil.*, 2nd series, vi. 287), and which include 2 atoms of water. (THOMSON.)

CHROMATE OF POTASSA. ($chr' + P$).—This salt is prepared by exposing a mixture of 4 parts of powdered native chromite of iron with 1 of nitre, to a strong heat for some hours, and washing out the resulting soluble matter; the process is repeated till the ore is decomposed. The washings yield *chromate of potassa* by evaporation. Dumas directs equal parts of nitre and of the pulverized ore to be heated gradually to redness; nitric oxide is disengaged, and chromate, silicate, aluminate, and sometimes manganate of potassa, are produced, forming a porous mass: the oxide of iron is set free; the chromate of potassa is washed out, and the residue, which still contains chromium, may be digested in dilute hydrochloric acid, which dissolves the oxide of iron and alumina, and again heated with nitre. The washings are to be exactly neutralized by nitric acid, which

separates the alumina and silica on evaporation; the crystals of chromate are then separated from those of nitrate of potassa, and purified by recrystallization. Dumas observes that the chromates might be abundantly obtained at a moderate price if the American chromates of iron were decomposed there by the nitrate of soda of Peru.

Chromate of potassa forms yellow crystals, the primary form of which is a right rhombic prism. (BROOKE, *Ann. of Phil.*, 2nd series, vi. 120.) It has a disagreeable metallic taste. It is extremely soluble in boiling water. At 60°, 100 parts of water dissolve about 48 of the salt. It is insoluble in alcohol. Its specific gravity is 2·6. It is anhydrous, and its colouring power is so great, that 1 part gives colour to 40,000 of water. (THOMSON.) If 1 grain be dissolved with 20 of nitre, and the solution evaporated, the crystals of nitre are almost as yellow as those of the chromate. When heated to redness it acquires a crimson colour, but becomes again yellow on cooling. When fused, it becomes green from loss of oxygen. (*Ann. of Phil.*, xvi. 321.) Heated with acetic acid and alcohol it is converted into acetate of potassa, and acetate of protoxide of chromium. (TASSAERT, *Ann. de Ch. et Ph.*, xxii. 51.) As it occurs in commerce it is sometimes blended with sulphate of potassa, and as these salts are isomorphous they are with difficulty separable. It consists of

		Tassaert. Thomson.	
Potassa	1 . . 48	. . .	48
Chromic acid	1 . . 52	. . .	52
<hr/> Chromate of potassa		<hr/> 1	<hr/> 100
			100

BICHRIMATE OF POTASSA ($\frac{2}{3}$ *chr'* + P) is obtained by adding a sufficiency of sulphuric or other acid to a solution of the chromate to give it a sour taste, and setting it aside for a day or two, when deep orange-coloured or red crystals are deposited; the acid abstracts half the potassa, and if sulphuric acid be used, there is some difficulty in separating the sulphate from the chromate; nitric acid is preferable, but the purest salt is obtained when acetic acid is used. The crystals are in the form of anhydrous quadrangular prisms and tables, permanent in the air, of a cooling metallic taste, soluble in 10 parts of water at 60°, and much more soluble in boiling water. Their specific gravity is 1·98. At a red heat, they fuse, without decomposition, into a transparent red liquid. At a white heat, half the acid of the salt is decomposed, forming a mixture of oxide of chromium and neutral chromate of potassa. This salt is largely manufactured at Glasgow, for the use of calico-printers. It consists of

		Grouvelle:		Thomson.	Tassaert.
Potassa	1 . 48 . 31·6	. 31·154	. 31·579	. 32·6	
Chromic acid	2 . 104 . 68·4	. 68·846	. 68·421	. 67·4	
<hr/> Bichromate of potassa		<hr/> 1	<hr/> 152	<hr/> 100·0	<hr/> 100·0
			100·000	100·000	100·0

BICHRIMATE OF CHLORIDE OF POTASSIUM.—When 2 atoms of chromic acid and 1 of chloride of potassium are dissolved in hydrochloric acid, crystals may be obtained from the solution, which are in the form of flat quadrangular prisms, having the colour of the bichromate of potassa. The same salt is formed when a mixed solution of bichromate of potassa and

hydrochloric acid is boiled; in that case, the requisite chloride of potassium is formed at the expense of the hydrochloric acid and potassa. This salt is permanent in the air, and may be dissolved without decomposition in dilute hydrochloric acid; but, by pure water it is again resolved into hydrochloric acid and bichromate of potassa. In this compound, therefore, the chloride of potassium acts as a *base* to the chromic acid. Peligot has obtained similar bichromates of the chlorides of sodium, calcium, magnesium, and ammonium. (*Ann. de Ch. et Ph.*, lii. 267.) The chlorobichromate of potassium consists of

Chromic acid	2	104	57.8	Peligot. 58.21
Chloride of potassium	1	76	42.2	41.29
Chromochloride of potassium	1	180	100.0	99.50

CHROMATE OF SODA (*chr'* + S) crystallizes in oblique rhombic prisms, efflorescent in dry air (BROOKE, *Ann. of Phil.*, 2nd series, vi. 287), and of a fine yellow colour, very soluble in water, and sparingly so in alcohol: they consist of 1 atom of anhydrous chromate + 12 atoms of water. The *bichromate of soda* is red, and forms large irregular plates, consisting of 1 atom of anhydrous bichromate + 20 atoms of water. (THOMSON.)

CHROMATE OF LITHIA (*chr'* + L) forms yellow oblique prisms very soluble in water. (C. GMELIN.)

CHROMATE OF LIME. (*chr'* + C.)—When chromate of potassa is mixed with solution of chloride of calcium, a yellow precipitate gradually falls: the salt described by Vauquelin as forming silky crystals, is probably a *bichromate of lime*.

CHROMATE OF BARYTA (*chr'* + B) is a pale yellow powder which falls when chromate of potassa is dropped into chloride of barium: it is very sparingly soluble in water, but soluble in nitric and hydrochloric acids, and in excess of chromic acid, and again precipitable by ammonia. (GMELIN.) It consists of

Baryta	1	77	59.7	Vauquelin. 57.75	Berzelius. 59.85
Chromic acid	1	52	40.3	42.25	40.15
Chromate of baryta	1	129	100.0	100.00	100.00

CHROMATE OF STRONTIA. (*chr'* + STR.)—An insoluble pale-yellow powder: it dissolves in nitric, hydrochloric, and chromic acids. (GMELIN.)

CHROMATE OF MAGNESIA (*chr'* + M) may be formed by dissolving magnesia in chromic acid; it forms transparent rhomboidal crystals, very soluble in water, and containing 1 atom of anhydrous chromate + 2 atoms of water. (THOMSON.)

CHROMATE OF MANGANESE.—Neither chromate nor bichromate of potassa produce any immediate precipitate in solutions of the protoxide of manganese, but after a time a brown precipitate falls: the chromic acid appears to be partially deoxidized by the oxide of manganese. Carbonate of manganese is soluble in chromic acid; the solution is brown and has an austere metallic taste; it is uncrystallizable, and decomposed by eva-

poration, a black powder being deposited, which is a chromite of sesquioxide of manganese. (DUMAS.)

CHROMATE OF IRON.—No combination of the protoxide of iron with chromic acid can exist, because it abstracts oxygen from that acid, and produces oxide of chromium. The chromate of the peroxide of iron (*perchromate*) is soluble: and there is a brown insoluble subchromate. The compound called *native chromate of iron*, is a compound of oxide of chrome with protoxide of iron: its specific gravity is 4.6. It sometimes forms octoëdral crystals: it is not soluble in the dilute acids, but may be decomposed by fusion with potassa, or with nitre, as above stated.

CHROMATE OF ZINC.—Chromate of potassa throws down a yellow flocculent precipitate in solution of sulphate of zinc, soluble in excess of the latter salt, and sparingly soluble in water. According to Thomson, this is a dichromate; there is also formed at the same time a double sulphate of potassa and zinc. (*Inorg. Chem.*, ii. 617.)

CHROMATE OF TIN.—Protoxide of tin decomposes chromic acid. *Perchromate of tin* is thrown down as a yellow precipitate when perchloride of tin is mixed with chromate of potassa.

CHROMATE OF CADMIUM may be obtained by mixing solutions of sulphate of cadmium and chromate of potassa; it falls in the state of a beautiful yellow powder which has little or no taste, and yet is not absolutely insoluble in water: it consists of 1 atom of chromic acid + 1 of oxide of cadmium + 5 of water. (THOMSON.) The temperature at which this hydrated salt was dried is not stated.

CHROMATE OF COBALT is a gray or brownish insoluble powder, precipitated on mixing solutions of chromate of potassa and nitrate of cobalt.

CHROMATE OF NICKEL is a red deliquescent salt; the alkalis throw down from it a *subchromate* of an orange colour. (BERZELIUS.) When solutions of chromate of potassa and sulphate of nickel are mixed together, no precipitate appears at first, but a reddish brown powder gradually falls, the quantity of which is increased by concentrating the liquid; when washed and dried, it is a rather beautiful reddish brown powder, destitute of taste, and not affecting vegetable blues: its constituents are 1 atom of chromic acid + 1 of protoxide of nickel + 4 of water. (THOMSON.)

CHROMATE OF COPPER.—When solutions of chromate of potassa and sulphate or chloride of copper are mixed, a buff-coloured precipitate falls: it is soluble in ammonia, with a fine green colour. It has a slightly sweet taste, and is sparingly soluble in water; it consists, according to Thomson, of 1 atom of chromic acid + 1 of oxide of copper + 2 of water.

CHROMATE OF LEAD. (*chr' + PL.*)—When chromate of potassa is added to any of the soluble salts of lead, a fine yellow powder falls, which is the neutral chromate; it is insoluble in water, but soluble in nitric acid, and in solution of potassa: solution of carbonate of potassa forms with it carbonate of lead and chromate of potassa: hydrochloric acid forms with it chloride of lead, and a hydrochloric solution of chromic acid: when heated its colour is deepened, and it fuses at a red heat. (VAUQUELIN.)

If the heat be continued, it is converted into oxide of lead and oxide of chrome (chromite of lead?). It is decomposed by sulphuric acid, and chromic acid is set free; if the acid be concentrated, sulphate of chromium is formed. Sulphate of lime and sulphate of lead are common contaminations of the chromate of lead of commerce. A diluted solution of nitrate of lead being added to a very alkaline solution of chromate of potassa, and left at rest for some time, there was found in the mixed solution, small red crystals, which, upon examination, proved to resemble in all their characters the native chromate of lead. (FARADAY.)

Native Chromate of Lead is of a deep orange-red colour: when pulverized, orange-yellow. It occurs crystallized in many varieties of form, of which the *primitive* is, according to Haüy, an oblique prism: it is somewhat translucent and brittle. Specific gravity 6. Before the blow-pipe it crackles, and melts into a grayish slag. It occurs in the gold mine of Beresof, in Siberia, in a vein traversing gneiss and mica slate; and near the same place in fissures in a sandstone. (W. PHILLIPS.) Chromate of lead is anhydrous, and consists of

					Pfaff.	Berzelius.		
					<i>Native.</i>	<i>Native.</i>	<i>Artificial.</i>	
Oxide of lead . . .	1	112	68.29		67.91	68.38	68.147	
Chromic acid . . .	1	52	31.71		31.72	31.62	31.853	
Chromate of lead	1	164	100.00		99.63	100.00	100.000	

DICHROMATE OF LEAD. SUBCHROMATE OF LEAD. (*chr'* + 2 PL.)—This salt was first noticed by Dulong and Grouvelle, in 1812 and 1822, and its composition pointed out by Badams in 1825 (*Ann. of Phil.*, 2nd series, ix. 303). It is formed by digesting the neutral chromate in caustic potassa; or by boiling a mixture of the neutral chromate with two-thirds its weight of oxide of lead, in water: it is an insoluble scarlet-coloured powder, which, when digested in acetic acid, loses half its oxide. Liebig and Wöhler prepare it by adding the neutral chromate to fuse nitre, and washing the residue. (POGGEND., xxi. 580.) It is anhydrous, and consists of

					Badams.		
Oxide of lead . . .	2	224	81.16		80.98		
Chromic acid . . .	1	52	18.84		19.02		
Dichromate of lead	1	276	100.00		100.00		

These chromates of lead are valuable pigments, and used both in oil and water colours, in calico printing, and dyeing. (LASSAIGNE, *Ann. de Ch. et Ph.*, xv. 76.)

The mineral called *Vauquelinite* is a double chromate of lead and copper, having, according to Berzelius, the formula ($2 \text{ PL} + \text{Cu} + 3 \text{ chr'}$).

CHROMATE OF ANTIMONY.—Chromate of potassa added to a hydrochloric solution of oxide of antimony forms a brown precipitate, soluble with a green colour in excess of the antimonial solution.

CHROMATE OF BISMUTH is formed by mixing chromate of potassa with nitrate of bismuth; it is a lemon-coloured powder, very sparingly soluble in water, and reddened by solution of potassa. (GROUVELLE.)

CHROMATE OF URANIUM.—Chromate of potassa occasions an ochre-yellow precipitate in solution of nitrate of uranium. (MOSER.) Carbonate of uranium dissolved by chromic acid yields small cubic and dendritic crystals. (JOHN.)

CHROMATE OF MOLYBDENUM.—When chromic and molybdic acids are dissolved in boiling-water, they form a yellow solution, which yields on evaporation an uncrystallizable residue, with which water forms a brown solution, and leaves a yellow and difficultly-soluble powder. (BERZELIUS.)

CHROMATE OF CHROMIUM.—When hydrated oxide or carbonate of chromium are digested in chromic acid, a solution is obtained of a brown colour, which is not decomposed by boiling, and which leaves on evaporation a deliquescent resin-like residue, soluble without decomposition in cold alcohol, and not precipitated by carbonic acid; it consists of 4 atoms of chromic acid + 1 of protoxide of chromium. (MAUSS.)

CHLORIDE OF CHROMIUM. SESQUICHLORIDE OF CHROMIUM. (*chr* + $\frac{1}{2}$ *c*.)—This compound is obtained by red-heating a mixture of dry protoxide of chromium and charcoal in a current of dry chlorine; a pink crystalline sublimate gradually rises, soft to the touch, and transparent when in thin layers. It slowly dissolves in water, and yields a green solution similar to that obtained by dissolving the hydrated protoxide of chrome in hydrochloric acid; or by decomposing chromate of lead by hydrochloric acid mixed with a little alcohol. When this aqueous solution of the chloride is evaporated, a dark-green *hydrated chloride* remains (composed of 2 atoms of sesquichloride and 3 of water), and when this is heated to about 500° out of the contact of air, it again becomes anhydrous and may be sublimed and condensed into a pale pink sublimate: heated in the air, it is partially decomposed in this state; it consists of

Chromium	1	28	34.1
Chlorine	$\frac{1}{2}$	54	65.9
Sesquichloride of chromium	1	82	100.0

PERCHLORIDE OF CHROMIUM. TERCHLORIDE OF CHROMIUM. (*chr* + 3 *c*.)—This compound may be obtained by distilling a mixture of chromate of lead, chloride of sodium, and concentrated sulphuric acid, and conducting the evolved vapour, which is a mixture of chlorine, hydrochloric acid, and terchloride of chromium, through a tube cooled to 0°, by which the latter is condensed into a dark-red liquid, heavier than water, very volatile, and exhaling fumes in the air, of the colour of nitrous acid. It acts violently on water, and produces a hydrochloric solution of chromic acid: it absorbs chlorine and dissolves iodine. A small fragment of phosphorus brought into contact with a drop of this compound, inflames and explodes; it is also rapidly decomposed by sulphur and by mercury: it decomposes ammonia with inflammation. (DUMAS and BERZELIUS.) It consists of

Chromium	1	28	20.6
Chlorine	3	108	79.4
Perchloride of chromium	1	136	100.0

OXICHLORIDE OF CHROMIUM, or a bichromate of perchloride of chromium, composed of 2 *chr*' + (*chr* + 3 *c*) or of (3 *chr* + 6 *o* + 3 *c*), has been

described by H. Rose. (See also a paper on this subject in the *Ann. de Ch. et Ph.*, LXvi. 387, by M. PH. WALTER.)

IODIDE OF CHROMIUM has not been examined.

BROMIDE OF CHROMIUM.—The solution of this salt is green when dilute, brown when concentrated; it has a sweet astringent taste, and yields a difficultly crystallizable and deliquescent residue when evaporated.

FLUORIDE OF CHROMIUM.—When protoxide of chromium is dissolved in hydrofluoric acid, and evaporated to dryness, a green crystallized salt remains, soluble in water. It forms difficultly-soluble double salts with the fluorides of ammonium, potassium, and sodium.

PERFLUORIDE OF CHROMIUM. TERFLUORIDE OF CHROMIUM. (*chr* + $\bar{3}f$).—This compound was discovered by Unverdorben in 1824. (TROMMSDORF's *Journal der Pharmacie*, ix., and *Edin. Journal of Science*, iv.) He obtained it by the process above described, under the head of *chromic acid*, and it is the red vapour there mentioned (p. 909). In consequence of its powerful action on glass, the gas can only be collected and preserved in vessels of platinum, so that its properties have been but imperfectly studied: it explodes when mixed with ammonia, and it seems doubtful whether it forms compounds with that gas, analogous to the fluoboric and fluosilicic acids. The action of water on this compound has been above adverted to: it appears to be composed of

Chromium	1	28	34.1
Fluorine	3	54	65.9
<hr/>					
Terfluoride of chromium	1		82		100.0

Hence, when decomposed by the action of water, 1 atom of this fluoride is resolved into 1 atom of chromic acid (*chr* + $\bar{3}o$), and 3 atoms of hydrofluoric acid ($\bar{3}h + f$).

NITRATE OF CHROMIUM.—When hydrated protoxide of chromium is dissolved in nitric acid, the solution is blue by reflected, but red by transmitted light: evaporated to dryness, a red deliquescent uncrystallizable salt (deutonitrate of chromium) remains. A solution of chromic acid in nitric acid yields on evaporation dark brownish-red granular crystals.

SULPHURET OF CHROMIUM is formed by passing the vapour of sulphuret of carbon through a red-hot porcelain tube, containing protoxide of chromium; or by heating a mixture of hydrated protoxide and sulphur, in vacuo: it is of a dark-gray colour, and when heated in the air it burns into oxide, evolving sulphurous acid: nitrohydrochloric acid converts it into a sulphate of the protochloride of chromium. It is insoluble in potassa and in sulphuret of potassium. This sulphuret is a weak *sulphur base*, and forms a few sulphur salts. It consists of

Chromium	1	28	53.85	54
Sulphur	$1\frac{1}{2}$	24	46.15	46
<hr/>							
Sulphuret of chromium	1		52		100.00		100

Rose and
Berzelius

SULPHITE OF CHROMIUM.—Sulphurous acid readily dissolves the hydrated protoxide.

SULPHATE OF CHROMIUM.—When hydrated protoxide of chromium is dissolved in dilute sulphuric acid a green solution is obtained, and on evaporation an insoluble *subsalt* remains.

AMMONIA-SULPHATE OF CHROMIUM.—This salt forms purple octoëdral crystals. (HAIDINGER, *Edin. Jour. of Science*, i. 100.)

POTASSA-SULPHATE OF CHROMIUM.—When a mixed solution of acid protosulphate of chromium, and sulphate of potassa, is left to spontaneous evaporation, regular octoëdral crystals, appearing purple in one direction, and green in another, are deposited. When this salt is dissolved in water, and the solution evaporated, it can only be again obtained in regular crystals, when excess of sulphuric acid is present, by which the solubility of the salt is diminished. This salt, Berzelius observes, may be called *chrome alum*, and if aluminum were substituted for chromium, common alum would be the result; so that there are not less than four isomorphous oxides which give aluminoid salts with potassa and sulphuric acid, namely, those of aluminum, manganese, iron, and chromium. It consists of

	Berzelius.			
Potassa	1	48	9.52	9.38
Protoxide of chromium	2	80	15.87	15.90
Sulphuric acid	4	160	31.75	31.80
Water	24	216	42.86	42.92
Potassiosulphate of chromium	17	504	100.00	100.00

CHROMOSULPHATE OF POTASSA.—When solutions of chromate and of sulphate of potassa are mixed and evaporated, a double salt is obtained, containing 43.3 of chromate and 56.7 of sulphate of potassa; it forms pale yellow prismatic crystals, and yields a precipitate with nitrate of baryta, which is only partially soluble in nitric acid. It has occasionally been substituted for chromate of potassa. It has a bitterish taste and is readily soluble in cold and hot water. (BOUTRON—CHARLARD, *Journal de Pharm.*, ix. 184.)

PHOSPHURET OF CHROMIUM.—When phosphate of chromium is intensely heated with charcoal a gray phosphuret is obtained. When phosphuretted hydrogen gas is passed over sesquichloride of chromium at a red heat, a black phosphuret is the result, which burns before the blow-pipe, and is insoluble in hydrochloric acid. (ROSE.)

PHOSPHATE OF CHROMIUM.—When phosphate of potassa is added to a solution of protochloride of chromium a gray precipitate falls. The solution of hydrated protoxide of chromium in phosphoric acid is emerald green and uncrystallizable. (VAUQUELIN.)

CARBONATE OF CHROMIUM.—The gray-green precipitate which the carbonated alkalis produce in solutions of the protosalts of chromium, is not a true carbonate, but a compound of subcarbonate and hydrate of protoxide of chromium. (BERZELIUS.) It dissolves, according to Meissner, in solution of carbonate of potassa, forming a grass-green liquid. It is sparingly soluble in carbonate of ammonia.

ARSENATE OF CHROMIUM.—When mixed solutions of arseniate of soda and protochloride of chromium are evaporated to dryness, and the residue digested in water, an insoluble green powder remains, composed

(THOMSON) of 1 atom of arsenic acid + 1 of protoxide of chromium. When hydrated oxide of chromium is digested in an aqueous solution of arsenic acid, a dark-green liquid is formed which leaves a green insoluble residue on evaporation: when heated red-hot it becomes rose-red, but buff coloured on cooling: according to Thomson, it is a *binarsenate of chromium*.

MOLYBDATE OF CHROMIUM.—A green precipitate falls when solutions of chloride of chromium and molybdate of potassa are mixed.

ALLOYS OF CHROMIUM.—Nothing is known of the alloys of chromium with the light metals: nor with manganese. With *iron*, it apparently unites in all proportions: this alloy is obtained by strongly heating mixtures of the oxides of chromium and of iron in a covered charcoal crucible. An alloy of 4 atoms of chromium with 1 of iron is crystalline and whiter than platinum, very hard and brittle. Steel containing from 1 to 2 per cent. of chromium answers well for cutting instruments. (BERTHIER, *Ann. des Mines*, vi. 579.) The other alloys of chromium have not been examined.

GENERAL CHARACTERS OF CHROMIUM.—The peculiar characters of the combinations of chromium, of the salts of the protoxide, and of the chromic acid, will be sufficiently evident from their preceding enumeration. Before the blowpipe, the oxide of chromium exhibits the following properties: it is fusible with microcosmic salt in the interior flame into a glass, which at the instant of its removal from the flame is of a violet hue, approaching more or less to dark blue or red, according to the proportion of the chromium. After cooling, the glass is bluish-green, but less blue than copper glass. In the exterior flame the colour becomes brighter, and less blue than the former. With borax it forms a bright-yellowish or yellow-red glass in the exterior flame; and in the interior flame this becomes darker and greener, or bluish-green.

§ XXVII. VANADIUM.

THIS metal was discovered by Sefström in the year 1830; its name is derived from *Vanadis*, a Scandinavian deity; he found it in the ores of iron from Taberg in Sweden, and in the slags from the reducing furnaces. The same metal was shortly after found by Mr. Johnston of Durham, in a lead ore from Wanlock-head; and by Del Rio, in a lead ore from Zemapán in Mexico: the latter terms it *Erythronium*, from the red colour of its acid. Thus have three persons noticed the existence of vanadium without the knowledge of each other's labours, but the merit of being its discoverer is due to Sefström. (*Phil. Mag. and Ann.*, x. 321; *Ann. de Ch. et Ph.*, xlvii. 377; BREWSTER'S *Journal*, v. 318, N. S.; POGGENDORFF'S *Ann.*, xxii. 1.)

Vanadium is most readily obtained from the native *vanadate of lead*, by the following process of Mr. Johnston: the ore is dissolved in nitric acid, and a current of sulphuretted hydrogen passed through the solution, by which lead and arsenic are precipitated, and a blue solution is obtained, which is evaporated to dryness; the residue is dissolved in ammonia, and a piece of sal-ammoniac larger than it can dissolve is introduced into the solution; *vanadate of ammonia* then subsides in the form of a white

powder, which should be washed, first with a solution of sal-ammoniac (in which it is insoluble), and then with alcohol of the specific gravity 0.86. This salt may be decomposed by heating and stirring it in a platinum crucible till it acquires a red colour; it is then *vanadic acid*. Berzelius succeeded in reducing this acid by the action of potassium, which at a moderate heat suddenly decomposes it, and on washing the residue, vanadium remains in a pulverulent form. Vanadium may also be obtained by decomposing the liquid chloride of vanadium by a current of dry ammonia, and heating the white saline mass which is so produced.

Vanadium has somewhat of a silvery lustre, is extremely brittle, conducts electricity, and is not acted upon by air or water at common temperatures; at a dull red-heat it takes fire and burns into a black oxide; it is not acted upon by sulphuric, hydrochloric, or hydrofluoric acids, but nitric and nitrohydrochloric acids yield dark blue solutions; it is not acted on by boiling caustic potassa, nor by the alkaline carbonates at a red heat: its equivalent is 68. (68.5 TURNER, 68.66 GRAHAM.)

VANADIUM AND OXYGEN.—There are three compounds of this metal with oxygen: two oxides, and an acid.

PROTOXIDE OF VANADIUM. ($va + o.$)—When a stream of dry hydrogen gas is passed over heated vanadic acid, water is formed, in consequence of the partial reduction of the acid, and a black substance remains, which is extremely infusible, conducts electricity, is strongly electronegative in relation to zinc, and which, when heated in the air, is converted by slow combustion into the deutoxide. It is not salifiable. From these characters, this substance, if not vanadium, would appear to be a mixture of the metal with a portion of the oxide: according to Berzelius it is a compound of 68 vanadium + 8 oxygen, and therefore a *protoxide*. Exposed to air and moisture it slowly absorbs oxygen, and when kept in water gradually communicates to it a green tint: the same change occurs in alkaline and acid solutions, and with the exception of nitric and nitrohydrochloric acids, it is not dissolved by them.

DEUTOXIDE OF VANADIUM. ($va + 2 o.$)—When 10 parts of protoxide and 12 of vanadic acid are intimately mixed and heated in an exhausted vessel, or in one filled with carbonic acid, a black compound is obtained, which is insoluble in water, and which consists of 68 vanadium + 16 oxygen. This is the only salifiable oxide: it may be obtained in the state of *hydrate*, by precipitation from its acid solutions by carbonate of soda, and if carefully dried out of the contact of air is of a gray colour, and gives out its water when heated. In this hydrated state it yields blue solutions with the acids: it also dissolves in caustic potassa and in ammonia, forming brown liquids.

VANADIC ACID. ($va + 3 o.$)—When vanadate of ammonia is moderately heated and stirred in an open vessel, it gradually acquires a red colour, and leaves vanadic acid: heated in a close vessel, the hydrogen of the ammonia deoxidizes the acid, and the deutoxide is the product; vanadic acid, when fused, is red, but when in powder, brown. it fuses at a heat below redness, and in the act of crystallizing, as it cools, it

contracts in bulk, and gives out so much latent heat as to become incandescent. It undergoes no change by heat, provided all deoxidizing agents are excluded; when any combustible matter is present, it passes into the state of oxide: it is tasteless, insoluble in alcohol, and nearly so in water. The equivalent of vanadic acid is 92. It consists of

Vanadium	1	68	74
Oxygen	3	24	26
Vanadic acid	1	92	100

VANADIATES.—The compounds of vanadic acid with salifiable bases are generally orange-coloured or yellow, but they sometimes are produced colourless, without any apparent change of composition: it forms neutral and bi-salts, those with the alkalis being soluble, and with the other oxides, either sparingly soluble or insoluble. The soluble salts are easily deoxidized, by alcohol, sulphuretted hydrogen, sulphurous acid, and several of the hydracids. Vanadic acid dissolves and forms variously coloured compounds with the deutoxide of vanadium: these compounds are formed when the deutoxide in water is exposed to air; it gradually forms vanadic acid, and the solution becomes blue, green, yellow, and red, according to the extent of acidification. It also combines with some of the other acids, as is the case with the chromic acid.

The colour of vanadic acid distinguishes it from others, with the exception of the chromic, with which it was at first confounded; but the *blue* colours, as opposed to the green of chromic acid, produced by deoxidizing substances, is a distinctive character. When heated with borax before the blowpipe it produces, like chromic acid, a green bead in the reducing flame; but in the exterior flame, the green remains if from chrome, but becomes yellow if from vanadium.

SALTS OF VANADIUM.—The salts of the deutoxide of this metal are best obtained by the action of the respective acids upon the hydrated deutoxide: they are blue, and afford a gray precipitate with the alkalis, which when exposed to air becomes red: infusion of galls blackens them. The *nitrate of vanadium*, which is at first blue, becomes red during evaporation, from the formation of vanadic acid.

CHLORIDES OF VANADIUM.—When deutoxide of vanadium is digested in hydrochloric acid, a brown compound is obtained, which appears to be a *bichloride* ($va + 2c$). When dry chlorine is passed over a red-heated mixture of protoxide of vanadium and charcoal, in a glass or porcelain tube, a yellow liquid is obtained, which when acted upon by water yields hydrochloric and vanadic acids; it is therefore a *terchloride* ($va + 3c$). By the action of hydriodic, hydrobromic, hydrofluoric, and hydrocyanic acids upon the oxide, an *iodide*, *bromide*, *fluoride*, and *cyanuret* of vanadium may be obtained.

SULPHURETS OF VANADIUM.—By passing a current of sulphuretted hydrogen over the deutoxide heated to redness, a *bisulphuret of vanadium* is ultimately obtained. The same compound is formed when sulphate of ammonia is mixed with a solution of a salt of vanadium, till the precipitate first formed is redissolved, and then, decomposing the deep purple

solution by sulphuric or hydrochloric acid: a brown bisulphuret subsides, which becomes black when it is dried. In the hydrated state it is dissolved by the alkalis and alkaline sulphurets, but is insoluble in the acids, with the exception of the nitric and nitrohydrochloric, by which it is converted into sulphate. When sulphuretted hydrogen is passed through vanadic acid in water, a mixture of hydrated deutoxide and sulphur is precipitated; but when a solution of vanadic acid in hydrosulphuret of ammonia is acidulated by hydrochloric or sulphuric acid, a hydrated *tersulphuret* subsides; its colour is at first light brown, but it becomes almost black by drying, and when heated to redness in close vessels, it gives off water and sulphur, and is resolved into the bisulphuret. It dissolves in alkalis and in alkaline sulphurets.

PHOSPHURET OF VANADIUM.—When phosphate of vanadium mixed with a little sugar is exposed to a white heat, a gray phosphuret is obtained. (TURNER'S *Elements*, 577, *et seq.*)

§ XXVIII. TUNGSTEN.

THIS metal, which has also been called *Scheelium* and *Wolframium*, was first obtained by Messrs. de Luyart, from the *tungstic acid* previously discovered by Scheele, in 1781. Its native sources are *wolfram*, which is a tungstate of iron and manganese; and the *tungstate of lime*. It is obtained by exposing a mixture of tungstic acid and charcoal to a red heat, or by passing hydrogen over the ignited acid. It is very difficult of fusion, very hard, brittle, and of an iron colour. Its specific gravity 17.4. Its approximate specific heat is 0.03636. (REGNAULT.) By the action of heat and air, tungsten is converted into an oxide, which is of a yellow colour. It is also oxidized by nitric acid. It is gradually dissolved by solution of potassa, with the evolution of hydrogen, and a tungstate of potassa is produced. A piece of zinc immersed in a solution of tungstate of ammonia throws down metallic tungsten in the form of a brown powder. (DUMAS.) The equivalent of tungsten may be assumed at about 100. (94.8 GRAHAM, 96 GMELIN, 99.7 TURNER.)

OXIDE OF TUNGSTEN. DEUTOXIDE OF TUNGSTEN ($tu + 2o$) may be obtained by mixing finely-powdered wolfram with twice its weight of carbonate of potassa, and fusing it in a platinum crucible. Tungstate of potassa is thus formed, which is dissolved in hot water, with half its weight of sal-ammoniac, evaporated to dryness, and heated red-hot in a Hessian crucible. The mass is then well washed in boiling water, and digested in weak solution of potassa. The residue is oxide of tungsten. In this process the tungstate of potassa and sal-ammoniac form chloride of potassium and tungstate of ammonia; but at a red heat the ammonia decomposes the tungstic acid, and reduces it to the state of oxide, which is prevented by the fused chloride of potassium from passing into the state of acid. (WÖHLER, *Quarterly Journal*, xx. 177.) Thus prepared, the oxide is black, and when heated to redness, it suddenly ignites, and becomes converted into tungstic acid by the absorption of oxygen. It does not appear capable of entering into combination with the acids so as

to form salts. When a current of hydrogen gas is carefully passed over heated tungstic acid, it is partially deoxidized and converted into a chocolate-coloured oxide, which neither combines with acids nor with bases, and which is identical in composition with the above. (*Ann. de Ch. et Ph.*, xvii. 16.) If the action of hydrogen be too long continued, the oxide itself is reduced. This oxide consists of

				Berzelius.
Tungsten . . .	1 . .	100 . .	86.21 . .	85.54
Oxygen . . .	2 . .	16 . .	13.79 . .	14.46
Oxide of tungsten	1	116	100.00	100.00

Wöhler has described an interesting combination of this oxide with soda, which is obtained by adding as much tungstic acid to fused tungstate of soda as it will dissolve, and then passing hydrogen over the compound at a red heat: on washing out the undecomposed tungstate with water, a golden-coloured substance remains, in small cubes and scales of a beautiful golden metallic lustre, and insoluble in caustic alkalis and in nitric, sulphuric, and nitrohydrochloric acids, but soluble in hydrofluoric acid. At a red heat, oxygen, chlorine, and sulphur, decompose it. It cannot be obtained by the direct combination of soda with the oxide. (POGGEND., ii. 345.) It consists of

				Wöhler.
Soda . . .	1 . .	32 . .	12 . .	12.4
Oxide of tungsten	2 . .	232 . .	88 . .	87.6
	1	264	100	100.0

TUNGSTIC ACID ($tu + 3O$) or tu' , is obtained when the oxide is heated red-hot, and stirred in an open vessel. When finely-powdered native tungstate of lime is boiled for some hours in nitric acid, tungstic acid is separated, in the form of a yellow powder, which may be freed from adhering nitric acid, by dissolving it in ammonia, and heating the tungstate of ammonia to redness. Tungstate of potassa, prepared by heating wolfram with carbonate of potassa, as above described, may also be decomposed by nitric acid, and the precipitate treated with ammonia as before. Tungstate of lime may also be decomposed by digestion in hydrochloric acid; chloride of calcium and tungstic acid are the results. In all cases where tungstic acid has been in contact with an acid, or where it is precipitated from its alkaline solutions by acids, the precipitate which falls retains traces of the foreign acid: hence the advantage of forming a tungstate of ammonia and decomposing it by heat only.

Tungstic acid is a yellowish powder, which appears green whilst hot, and also acquires a greenish colour by long exposure to the sun's rays. Its specific gravity is 6.12. It is insoluble in water, but readily soluble in the caustic alkalis, when in its hydrated state; after it has been heated it is very difficultly acted upon by solvents, but its compounds may be obtained by fusion at a red heat. When precipitated by the acids from its ammoniacal solution, a portion of the precipitant is carried down with it, and in this way compounds of sulphuric, nitric, and hydrochloric acids, with tungstic acid, may be produced, which are more or less soluble in water.

When tungstic acid is exposed to a heat of about 600° in a current of

hydrogen, it becomes blue; a similar product is obtained when metallic zinc is put into a mixture of hydrochloric and tungstic acids; or when tungstate of ammonia is decomposed by distillation in a retort. This has sometimes been regarded as a distinct oxide ($2tu + 5O$), (MALAGUTI, *Ann. de Ch. et Ph.*, LX. 271;) but according to Berzelius, it is a tungstate of the oxide, or a compound of the acid and oxide. Tungstic acid consists of

				De Luyart.	Bucholz.	Berzelius.
Tungsten	1	100	80.6	80.64	80	79.766
Oxygen	3	24	19.4	19.36	20	20.234
Tungstic acid	1	124	100.0	100.00	100	100.000

GENERAL PROPERTIES OF THE TUNGSTATES.—The alkaline and earthy tungstates are colourless: they are heavy; and those which are soluble have a bitter metallic taste; hydrochloric, nitric, and sulphuric acids occasion in them white precipitates; phosphoric acid forms with them soluble triple compounds. When their acid solutions are acted upon by zinc, they acquire the blue colour above adverted to. The tungstates which are not decomposed by heat are fusible.

TUNGSTATE OF AMMONIA is procured in crystalline scales, sparingly soluble in water, of a metallic taste, by digesting the acid in ammonia. It contains, according to Berzelius,

				Berzelius.
Ammonia	1	17	6.0	6.338
Tungstic acid	2	248	87.6	87.000
Water	2	18	6.4	6.662
Tungstate of ammonia	1	283	100.0	100.000

TUNGSTATE OF POTASSA is uncrystallizable (or very difficultly crystallizable) and deliquescent; it has a styptic and acrid taste. The acids occasion precipitates in its solution, which are triple compounds of tungstic acid, potassa, and the acid used as a precipitant. The *Nitro-tungstate of Potassa* is the salt originally described by Scheele as tungstic acid. It dissolves in 20 parts of water at 212° , and reddens litmus. Tungstate of potassa, when neutral, is not affected at high temperatures by hydrogen, but the acid tungstate has its excess of acid decomposed and reduced.

TUNGSTATE OF SODA crystallizes in hexaëdral tables, soluble in 4 parts of cold, and in 2 of boiling water, and of an acrid taste. Sulphuric, nitric, and hydrochloric acids occasion precipitates, as in the tungstate of potassa. *Bitungstate of Soda* is easily crystallizable and soluble in 8 parts of water at 60° . By hydrogen at a red heat it is reduced to neutral tungstate, and a compound of soda and oxide of tungsten, as above stated.

TUNGSTATE OF LIME, OF BARYTA, AND OF STRONTIA, are insoluble white compounds. *Native Tungstate of Lime* is the substance from which Scheele originally obtained tungstic acid; it generally accompanies tin ore in Bohemia, Saxony, and Cornwall: fine specimens have also been found in Cumberland: it is white or nearly so; its primary form is an octoëdron with a square base; its density about 6. It is constituted of

							<i>Native.</i>
							Berzelius.
Tungstic acid	. 1 . . .	124 . . .	81.6 . . .				80.417
Lime 1 . . .	28 . . .	18.4 . . .				19.400
<hr/>							
Tungstate of lime	1	152	100.0				99.817

TUNGSTATE OF MAGNESIA is obtained by boiling the acid with magnesia, filtering, and evaporating; it crystallizes in pearly scales. The acids produce precipitates of triple compounds in its solution.

TUNGSTATE OF MANGANESE, formed by adding tungstate of potassa to hydrochlorate of manganese, is an insoluble white powder. (JOHN, *Gehlen's Journal*, iv.) *Tungstate of Iron* is also insoluble. *Tungstate of Zinc and of Tin* have not been described, nor have any of the remaining tungstates been examined in their pure state.

Native Tungstate of Iron and Manganese, or *Wolfram*, commonly accompanies tin stone, and is found in Cornwall and in many of the tin mines of Saxony and Bohemia: it has also been found in Siberia, and in the United States of America; its colour is nearly black, and it occurs massive and crystallized, its primary form being a right oblique-angled prism: its specific gravity is 7.15. A specimen analyzed by Mr. Richardson, gave 73.60 tungstic acid, 11.20 protoxide of iron, 15.75 protoxide of manganese: these numbers are nearly the equivalents of 3 atoms of tungstate of iron, 4 atoms of tungstate of manganese. (THOMSON, *Mineralogy*, i. 487.)

CHLORIDES OF TUNGSTEN.—When metallic tungsten is heated in chlorine, it burns and forms a red crystalline compound, which is fusible and volatile, and which, according to Wöhler, becomes blue in water, forming hydrochloric acid, and depositing a suboxide. It is soluble in caustic potassa with the evolution of hydrogen, and yields tungstate of potassa and chloride of potassium. It consists of

Tungsten	1 . . .	100 . . .	58
Chlorine	2 . . .	72 . . .	42
<hr/>			
Chloride of tungsten	1	172	100

PERCHLORIDE OF TUNGSTEN. ($tu + 3c$).—When sulphuret of tungsten is heated in a current of chlorine, it burns, and forms a *perchloride*, which condenses in yellowish-white plates. This chloride, when gently heated, rises in the form of a dark-yellow vapour before it fuses: heated on a slip of platinum in the flame of a spirit-lamp, it is decomposed by the water of the flame, and yields hydrochloric and tungstic acids; the latter forms a luminous fume, and condenses in large light flocks. It consists of

							Malaguti.
							47.4
Tungsten	1 . . .	100 . . .	48.1 . . .				
Chlorine	3 . . .	108 . . .	51.9 . . .				54.6
<hr/>							
Perchloride of tungsten	1	208	100.0				100.0

According to H. Rose (*Ann. de Ch. et Ph.*, LXvi. 215), the compound obtained by heating oxide of tungsten in chlorine, is an *oxichloride of tungsten*, or a tungstate of chloride of tungsten, composed of $2(tu + 3o) + (tu + 3c)$, or of

Tungsten	3	300	65·8	H. Rose. 64·80
Oxygen	6	48	10·5	10·95
Chlorine	3	108	23·7	24·25
Oxichloride of tungsten	1	456	100·0	100·00

SULPHURETS OF TUNGSTEN.—When 1 part of tungstic acid is mixed with 6 of cinnabar, and heated intensely for half an hour; or when the vapour of sulphur, or sulphuretted hydrogen, is passed over tungstic acid heated intensely in a porcelain tube, a black powder is obtained, which assumes metallic lustre by friction, and which consists, according to Berzelius, of 100 tungsten + 33·6 sulphur: it is therefore a *bisulphuret* ($tu + 2s$).

When tungstic acid is dissolved in hydrosulphuret of ammonia, or of potassium, and precipitated by an acid, a compound falls of a dirty-yellow colour, and somewhat soluble in water; it becomes darker coloured when dried, and when heated in close vessels, first gives off a little water, and then its excess of sulphur; it leaves the bisulphuret. This appears to be a *tersulphuret* ($tu + 3s$).

PHOSPHURET OF TUNGSTEN may be formed, but has not been examined. (BERZELIUS.)

CHARACTERS OF THE COMPOUNDS OF TUNGSTEN.—The general properties and tests of tungsten and its compounds will be evident from the preceding details. Before the blowpipe, tungstic acid becomes upon charcoal at first brownish-yellow, is then reduced to a brown oxide, and lastly, becomes black without melting or smoking. With microcosmic salt it forms in the interior flame a pure blue glass, without any violet tinge; in the exterior flame this colour disappears, and appears again in the interior. With borax, in the internal flame, and in small proportion, it forms a colourless glass, which, by increasing the proportion of acid, becomes dirty-gray, and then reddish. By long exposure to the external flame it is rendered transparent, but as it cools it becomes muddy, whitish, and changeable into red when seen by daylight. It is not reduced. When *wolfram* is heated before the blowpipe, it first decrepitates, and, at a high temperature, fuses into a crystalline globule of metallic lustre; with borax it forms a green bead, and with biphosphate of soda it fuses into a deep red globule. Tungstate of lime, when heated by the blowpipe-flame, crackles and becomes opaque, but does not fuse; with borax, it fuses into a globule.

§ XXIX. COLUMBIUM.

THIS metal was discovered in 1801 by Mr. Hatchett, in a mineral from North America. It was afterwards found combined with the oxides of iron and manganese, and also with yttria, in the Swedish minerals called *tantalite* and *yttro-tantalite*. Tantalite is chiefly found in octoëdral crystals, and in masses of a black or gray colour, in Finland. Its specific gravity is 7·9, and it contains, according to Ekeberg, 80 oxide of columbium, 12 oxide of iron, and 8 oxide of manganese. Yttro-tantalite is found at Ytterby, in Sweden, in a rock of red felspar and mica; it is

usually in small masses, plates, or grains; there are three varieties which have been analyzed by Berzelius, with the following results:—

	Black.	Yellow.	Brown.
Columbic acid	57·00	60·124	51·815
Yttria	20·25	29·780	38·515
Lime	6·25	0·500	3·260
Tungstic acid	8·25	1·044	2·592
Peroxide of iron	3·50	1·155	0·555
Oxide of uranium	0·50	6·622	1·111
	95·75	99·225	97·848

There is also a mineral found near Cape Farewell, in East Greenland, and which has been called *Fergusonite*; it occurs crystallized in octoëdra and their modifications; its density is 5·7 to 5·8; its colour brownish-black; it was first described by Haidinger (*Edin. Phil. Trans.*, x. 274), and was analyzed by Hartwell; its constituents are

Columbic acid	47·75
Yttria	41·91
Protoxide of cerium	4·68
Zirconia	3·02
Oxide of tin	1·00
Oxide of uranium	0·95
Peroxide of iron	0·34
	99·65

Columbium was discovered in the Swedish minerals by Ekeberg, and, considering it as a *new* metal, he called it *tantalum*. In 1809 (*Phil. Trans.*) Dr. Wollaston re-examined these, and the specimen in the British Museum originally analyzed by Mr. Hatchett, and demonstrated the identity of columbium and tantalum. As the former name was given to this metal by its original discoverer, it is here retained.

Columbite and tantalite may be decomposed by the following process:—Mix 5 parts of the finely-powdered mineral with 25 of carbonate of potassa, and 10 of borax; fuse the mixture, and when cold, digest it in hydrochloric acid; this dissolves everything except the peroxide of columbium, which remains in the form of a white powder. (WOLLASTON, *Phil. Trans.*, 1809, p. 248.) From 5 grains of *columbite*, Dr. Wollaston obtained 4 grains of oxide of columbium, 0·75 of oxide of iron, and 0·25 of oxide of manganese; and from 5 grains of *tantalite* he procured 4·25 of oxide of columbium, 0·50 of oxide of iron, and 0·2 of oxide of manganese.

Berzelius obtained metallic columbium by heating potassium with the *potasso-fluoride of columbium*, and washing the reduced mass with water. It remains in the form of a black powder; by pressure it acquires lustre and the colour of iron; it burns at a red heat into a whitish oxide. Its specific gravity is about 6. It is insoluble, or nearly so, in hydrochloric, nitric, and nitrohydrochloric acids; but is acted on by hydrofluoric acid. Heated to redness, it burns into columbic acid. Mixed with nitre, and projected into a red-hot crucible, it detonates, and is oxidized. It forms alloys with other metals. (*Ann. de Ch. et Ph.*, iii. 140.) Its equivalent may be assumed as 185. (184 GMELIN, 185 TURNER.)

OXIDE OF COLUMBIUM.—When columbic acid is intensely heated for an hour and a half in a charcoal crucible, it is superficially reduced to a metallic state, but the interior portion is a dark-gray, and brown when pulverized; it is insoluble in the acids, but may be peroxidized by fusion with potassa: it burns when heated in the air: it consists of

				Berzelius.	
Columbium	1	185	92.04	92.02	
Oxygen	2	16	7.96	7.98	
<hr/>				<hr/>	
Oxide of columbium	1	201	100.00	100.00	

COLUMBIC ACID. (*col*+³0) or *col*.—The best process for obtaining columbic acid consists in fusing the ore of columbium with bisulphate of potassa, and proceeding as directed by Berzelius. (*Lehrbuch*.) An easier, but less economical process, is that of Ekeberg, in which the ore is finely powdered, and fused with caustic potassa; a soluble columbate of potassa is formed, from which the columbic acid may be precipitated, as a white *hydrate*, by the acids. Dr. Wollaston's process above given may also be used. The characters of columbic acid are very well marked. In its anhydrous state, after having been ignited, it is nearly insoluble in hydrochloric, nitric, and sulphuric acids; it is soluble in potassa, and carbonate of potassa; 8 grains of the latter, fused with 1 of the oxide, render it soluble in water. It is much less soluble in soda, and only retained while hot.

The hydrated columbic acid dissolves in nitric, hydrochloric, and sulphuric acids, and, according to Wollaston, in tartaric, citric, and oxalic acids. In this state, and whilst moist, it is abundantly soluble in solution of binoxalate of potassa, but scarcely at all in bitartrate of potassa. The oxalic solution is colourless; alkalis throw down the columbic acid; ferrocyanuret of potassium produces in it a yellow precipitate; infusion of galls gives it an orange colour, and when added in excess produces a precipitate; the hydrosulphurets occasion a white precipitate, with the evolution of sulphuretted hydrogen. Columbic acid consists of

				Berzelius.	
Columbium	1	185	88.5	88.49	
Oxygen	3	24	11.5	11.51	
<hr/>				<hr/>	
Columbic acid	1	209	100.0	100.00	

COLUMBATE OF AMMONIA is produced by digesting hydrated columbic acid in ammonia: it is insoluble, and at a red heat yields ammonia and water: the ammonia escapes by long exposure to air. Carbonate of ammonia only takes up a trace of columbic acid.

COLUMBATE OF POTASSA is obtained by fusing columbic acid with carbonate of potassa, pulverizing the product, and digesting it in water. The columbate of potassa, being nearly insoluble in a solution of carbonate of potassa, remains, and after it has been washed with a little cold water, it may be dissolved in boiling water; when this solution is distilled to dryness, a saline uncrystallizable mass remains, of an unpleasant metallic taste: its solution is precipitated by all the acids, not excepting the carbonic.

COLUMBATE OF SODA may be obtained as the preceding: it is less soluble, and is almost entirely deposited, as a white powder, during the cooling of its boiling aqueous solution.

COLUMBATE OF LIME and OF BARYTA are insoluble white powders.

FERRO-COLUMBATE OF MANGANESE has been adverted to above as a natural product, under the name of *columbite* or *tantalite*.

The remaining binary salts of the columbic acid with the oxides have not been examined.

CHLORIDE OF COLUMBIUM.—The metal burns when heated in chlorine, producing a yellow vapour, which condenses into a white pulverulent substance, which, on contact of water, is converted, with rapid action and increase of temperature, into hydrochloric and columbic acids: this is therefore a *terchloride* ($col + 3c$).

FLUORIDE OF COLUMBIUM.—When hydrated columbic acid is dissolved in hydrofluoric acid, and evaporated at a temperature of about 86° , crystals are obtained, which dissolve without residue in water, and which consist of fluoride of columbium and hydrofluoric acid. (BERZELIUS.) This compound combines with other fluorides to form *columbo-fluorides*.

SULPHURET OF COLUMBIUM.—When columbium is heated in the vapour of sulphur it burns into a sulphuret: a similar compound is formed by passing the vapour of sulphuret of carbon over columbic acid heated to whiteness in a porcelain tube. In the air this sulphuret burns into columbic acid, which obstinately retains a portion of sulphuric acid. Berzelius considers this as a *tersulphuret* ($col + s$).

The remaining combinations of columbium have not been sufficiently examined to require notice: the characters of its compounds will be evident from the preceding paragraphs.

§ XXX. MERCURY.

THE principal ore of this metal is the *sulphuret*, or *native cinnabar*, from which the mercury is separated by distillation with quicklime or iron-filings.

Mercury (γ) is a brilliant white metal, having much of the colour of silver, whence the terms *hydrargyrum*, *argentum vivum*, and *quicksilver*. It has been known from very remote ages. It is liquid at all common temperatures, solid and malleable at -40° , and contracts considerably at the moment of congelation. Its specific heat is 0.03332. (REGNAULT.) It boils and becomes vapour at about 670° . It emits vapour at all temperatures above 40° , but no apparent spontaneous evaporation goes on from it when below that temperature. (FARADAY.) Its specific gravity at 60° is 13.5. According to Kupfer the density of mercury at 39.2° is 13.5886; at 62.6° , 13.5569; at 78.8° , 13.535. In the solid state its density exceeds 14. The specific gravity of mercurial vapour is 6.976. (DUMAS, *Ann. de Ch. et Ph.*, xxxiii.) It is said to be sometimes adulterated with lead and bismuth, a fraud easily detected by the want of its due fluidity, and by its not being perfectly volatile, but leaving a residuum when boiled

in a platinum or iron spoon. The best method of purifying mercury is to redistil it in an iron retort, but such an operation is rarely necessary, for it is extremely pure as it occurs in commerce.

The equivalent of mercury is 200, (202 TURNER, 101 GMELIN, 100 THOMSON,) at least this number is most consistent with the binary compounds of the metal, and with the constitution of the salts of its oxides. Gmelin, in adopting the number 101, regards the protoxide and protochloride as a dioxide and dichloride; that is, ($2hg + o$) and ($2hg + c$.) Dr. Thomson also considers these compounds as a suboxide and subchloride. There are two circumstances which justify this atomic weight; one is, that the constant quantity obtained by multiplying the specific heat of mercury by its atomic number (see p. 163) requires that 100, or thereabouts, should be the equivalent; and the other, that the specific gravity of the vapour of mercury, in reference to hydrogen, is as 100 or 101 to 1.

Native Mercury occurs in small fluid globules, in most of the mines producing the ores of this metal.

MERCURY AND OXYGEN.—There are two oxides of mercury.

PROTOXIDE OF MERCURY. SUBOXIDE OF MERCURY. ($hg + o$).—This oxide is formed, when the protochloride of mercury is decomposed by triturating it in excess of solution of potassa, washing the product with cold water, and drying it at a common temperature in a dark place. (DONOVAN, *Ann. of Phil.*, xiv.) If heated, or exposed to the sun's rays, it is resolved into peroxide and metallic mercury. Thus prepared, the protoxide (or suboxide) of mercury is a dark gray or nearly black powder, insoluble in water, and yet having a metallic taste. Its density, according to Herapath, is 10.69. It was formerly prepared by agitating mercury and a little water for a long time together in contact of air; this was effected by tying a large phial containing a little mercury and water to the spoke of a mill wheel, and so leaving them to be shaken together; the small quantity of oxide thus obtained was called *Ethiops per se*. A preparation, often considered as nearly corresponding with this oxide, is directed in the *London Pharmacopœia*, under the name of *Hydrargyri oxidum cinereum*. It is made by boiling calomel with lime-water; but it is not a pure protoxide of mercury, and being uncertain in composition, is unfit for medical use. It is also supposed that the protoxide of mercury is contained in the *Pilula hydrargyri*, or *blue pill*, and in the *Unguentum hydrargyri*, or *mercurial ointment*. But these preparations are rather to be regarded as containing *finely-divided* mercury, and it is apparently obtained in a similar state when mercury is triturated with honey, mucilage, and other viscid bodies, and also with chalk, as in the *Hydrargyrum cum creta* of pharmacy: indeed, it is astonishing to what an extent mercury may be subdivided into extremely minute globules, so as to lose its metallic appearance even under a powerful magnifier; this is the case when solutions of mercury are precipitated by protochloride of tin: the metal then appears in the form of a gray powder, and remains in that condition while humid. "To obtain *precipitated mercury*, equal weights of crystallized protochloride of tin and corrosive sublimate may be dissolved, the first in diluted hydrochloric acid and the second in hot water, and the solutions mixed by stirring: the salt of tin assumes the

whole chlorine of the corrosive sublimate, becoming bichloride of tin, which remains in solution, while the mercury is liberated, and forms so fine a precipitate that it requires several hours to subside. It may be washed by affusion of hot water and subsidence, and slightly drained on a filter, but not allowed to dry. There can be no doubt that it is in this divided state, and not as the black oxide, that mercury is obtained by trituration with fat, turpentine, syrup, saliva, &c., in many pharmaceutical preparations." (GRAHAM.) Another mode of obtaining mercury in an extraordinary state of division was discovered by Mr. Daniell: it consists in agitating it in dilute sulphuric acid in contact with a few particles of sulphate of copper: in this case electrolytic actions are concerned; metallic copper is first precipitated and then oxidized, and hydrogen is given out upon the mercury, which appears to occasion it to assume the form of *froth*. It certainly seems very probable that, although mercury in its ordinary state is quite inactive as a medicine and passes through the bowels unaltered, it may be absorbed, and consequently prove active, when in the extremely comminuted form into which the preceding methods reduce it. Some of the protosalts of mercury, especially the protonitrate, when carefully prepared, and decomposed by excess of caustic potassa, furnish a precipitate of protoxide of mercury; it requires to be washed with repeated affusions of cold water and carefully dried, first on bibulous paper, and then in a vacuum over sulphuric acid. Guibourt regarded these precipitates as compounds of finely-divided mercury and peroxide, so that 1 atom of mercury and 1 atom of peroxide would constitute the supposed protoxide: at present, however, the existence of a true definite protoxide, forming the basis of the protosalts of mercury, is generally admitted; such an oxide is soluble in acetic acid, and the solution yields a black precipitate with potassa; whereas, acetic acid is without action on metallic mercury, however finely it may be divided. Those who regard the black oxide of mercury as a suboxide or dioxide, represent it by the formula ($2hg + o$): considered as a protoxide capable of forming definite salts by combination with 1 atom of the respective oxyacids, it will consist of

				Guibourt.	Donovan.	Fourcroy.	Seftstrom.
Mercury	1	200	96.2	95.69	96.04	96.16	96.2
Oxygen	1	8	3.8	4.31	3.96	3.84	3.8
Protoxide of mercury	1	208	100.0	100.00	100.00	100.00	100.0

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PEROXIDE OF MERCURY. ($hg + 2o$).—This oxide is produced by exposing mercury, heated nearly to its boiling-point, to the action of air. It becomes coated with reddish-brown scales, spangles, and crystals, and is ultimately entirely converted into a red crystallized mass, called in old pharmaceutical works, *precipitatum per se*, or *calcined mercury*. It is the *hydrargyri binoxydum* of the *London Pharmacopœia*. It is most easily obtained in a pure form, by introducing into a flat-bottomed matrass, of the annexed shape (fig. 278), about 8 ounces of mercury, and placing it in a sand-bath, heated nearly to the boiling-point of the metal. In about a month's time nearly the whole is converted into oxide, air being freely

admitted by the tube, while its length prevents the escape of mercurial vapour, which condenses and falls back into the body of the vessel; the remaining portion of running mercury may be driven off by exposing it in a basin to a heat below redness.

This oxide may also be obtained by evaporating nitrate of mercury to dryness, and carefully exposing the residue to heat. In this process 25 parts of mercury are dissolved in 35 of nitric acid, nitric oxide is abundantly disengaged, and on evaporation to dryness a pernitrate of mercury remains, which is carefully heated so long as fumes of nitrous acid are evolved; the resulting oxide is in the form of an orange-red crystalline powder, forming the *Hydrargyri nitrico-oxidum* of pharmacy. (See *Nitrate of Mercury*.)

A third mode of obtaining peroxide of mercury consists in adding excess of potassa to a solution of corrosive sublimate, or triturating corrosive sublimate in the alkaline solution: a yellow powder is thus thrown down, which is a *hydrated peroxide*; it loses its water at a moderate heat. If the potassa be not in considerable excess the precipitate is an oxichloride.

Peroxide of mercury has an acrid metallic taste, and is poisonous. According to Thomson, Guibourt, and Donovan, it is very sparingly soluble in water, and the solution has a metallic taste, and is rendered brown by sulphuretted hydrogen; other chemists deny the solubility of the perfectly pure peroxide, and ascribe its apparent solubility to the presence of a trace of the pernitrate. Its specific gravity is 11.074. When this oxide is heated, it acquires a black colour, but becomes again red on cooling; at a red heat it evolves oxygen, and is reduced to the metallic state: it was from this source that Priestley first obtained oxygen gas (see p. 64). When long exposed to light it becomes black upon the surface, in consequence, apparently, of superficial reduction to the state of protoxide. It should be entirely volatilized when placed upon a red-hot iron, for it is sometimes adulterated with red lead. Those who represent the black oxide by the formula ($^2hg + o$) consider this as a compound of 1 atom of mercury = 100 + 1 atom of oxygen = 8, or as ($hg + o$). In our system of equivalents it is a binoxide ($hg + ^2o$), and consists of

				Zaboarda.	Rose.	Proust.	Donovan.	Fourcroy.	Seftstrom.
Mercury . .	1	200	. 92.59	. 90	. 91	. 92	. 92.75	. 92.4	. 92.68
Oxygen . .	2	16	. 7.41	. 10	. 9	. 8	. 7.25	. 7.6	. 7.32
Peroxide of } mercury }	1	216	100.00	100	100	100	100.00	100.0	100.00

Both the oxides of mercury combine with the greater number of the acids, forming two distinct classes of salts, several of which are resolvable into salts with excess of base, and salts with excess of acid, so that the history of the saline combinations of mercury is thus rendered somewhat complex. There is also a great tendency to the formation of double salts among the haloid mercurial compounds; in short, mercury is, of all the metals, that which produces the most numerous and complicated series of saline combinations.

HYDRARGYRATE OF AMMONIA. AMMONIURET OF OXIDE OF MERCURY.
—When peroxide of mercury is digested in liquid ammonia a pale-yellow

compound of the peroxide with 13.6 per cent. of ammonia is obtained. (GUBOURT.) Dr. Kane considers this as a hydrated compound of amide of mercury and peroxide of mercury; but it may also be regarded as containing 1 atom of peroxide of mercury + 2 of ammonia.

MERCURY AND CHLORINE combine in two proportions, and form a protochloride and perchloride of mercury, corresponding in composition with the protoxide and peroxide. These compounds are often called *calomel* and *corrosive sublimate*. Those who regard the black oxide of mercury as a dioxide are of course obliged to represent calomel as a dichloride, or $(2hg + c)$, and corrosive sublimate as a protochloride, or $(hg + c)$; but consistently with our equivalents, calomel is $(hg + c)$ or a protochloride, and corrosive sublimate $(hg + 2c)$ or a bichloride or perchloride.

PROTOCHLORIDE OF MERCURY. SUBCHLORIDE OF MERCURY. CALOMEL. $(hg + c)$.—This compound is first mentioned by Crollius, early in the seventeenth century. The first directions for its preparation are given by Beguin, in the *Tyrocinium Chemicum*, published in 1608. He calls it *draco mitigatus*. Several other fanciful names have been applied to it, such as *aquila mitigata*, *manna metallorum*, *panchymagogum minerale*, *sublimatum dulce*, *mercurius dulcis*, &c. It is the *Hydrargyri chloridum* of the *London Pharmacopœia*.

There are two processes by which calomel is usually obtained: the one by the action of mercury on corrosive sublimate; the other by the mutual decomposition of protosulphate of mercury and chloride of sodium; the product is in both cases sublimed by heat. The first mode consists in triturating 4 parts of corrosive sublimate with 3 of mercury (and a little water to prevent the dust rising), until the globules disappear, and the whole assumes the appearance of an homogeneous gray powder, which is introduced into a matrass, placed in a sand-heat, and gradually raised to redness. The protochloride sublimes, mixed with a little of the perchloride, the greater part of which, however, being more volatile than the calomel, rises higher in the matrass; that which adheres to the protochloride may be separated, by reducing the whole to a fine powder, and washing in large quantities of hot distilled water. Pure protochloride of mercury, in the form of a yellowish-white insipid powder, remains. It was formerly the custom to submit this product to very numerous sublimations, under the idea of rendering it *mild*; but these often tended to the production of corrosive sublimate; and the calomel of the first sublimation, especially if a little excess of mercury be found in it, is often more pure than that afforded by subsequent operations.

In this process the operation consists in reducing the perchloride to the state of protochloride by the addition of mercury; it is objectionable on account of the heat required, and the destruction of the matrasses in which it is sublimed, so that some have proposed to substitute the *humid process*, as it is termed, by precipitation, as devised by Scheele and Chevenix. It is as follows: Form a *protonitrate of mercury* by dissolving as much mercury as possible in nitric acid; then dissolve in boiling water a

quantity of common salt, equal to half the weight of the mercury used, and render this solution sensibly sour by hydrochloric acid, and pour the hot nitrate of mercury into it. Wash and dry the precipitate. If this process be carefully performed, and the precipitate thoroughlyedulcorated, the calomel is said to be sufficiently pure; but a small portion of chloride of sodium remains combined with the calomel, which material affects its medical uses.

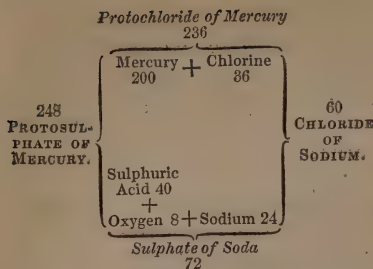
The second process, by sublimation, however, appears on the whole the least exceptionable for the production of this important article of pharmacy. It is as follows: Boil 2 pounds of mercury with 30 ounces of sulphuric acid in a glass vessel, until the sulphate of mercury is dry. When it has cooled, rub it with 2 pounds of mercury in an earthenware mortar, till they are well mixed. Then add $1\frac{1}{2}$ pounds of chloride of sodium, and rub them together until globules are no longer visible. Put this mixture into a proper vessel, and heat it gradually to redness; the protochloride of mercury, or calomel, sublimes, and condenses in various forms, according to the rapidity of the operation, and the form and capacity of the subliming vessel. If intended for medicinal use, it should be cautiously reduced to an impalpable powder, and washed with repeated affusions of hot distilled water, till it becomes perfectly tasteless, and till the water, in which it has been washed, is not discoloured by the addition of an aqueous solution of sulphuretted hydrogen.

This process has many advantages over the first method. The sulphate of mercury may be formed by boiling the metal with sulphuric acid to dryness in a cast-iron vessel, which should be conveniently arranged for the escape of the abundant fumes of sulphurous acid developed by the action of the mercury, and which are often a serious nuisance to the neighbourhood. They may be very effectually annihilated by suffering them to pass through a long flue and lofty chimney, mixed with abundance of coal smoke. The *persulphate* of mercury is triturated with a sufficient quantity of metallic mercury to convert it into a *protosulphate*, and then mixed with a due proportion of common salt, and subjected to sublimation. Protosulphate of mercury is a compound of

1	proportional of protoxide of mercury . . .	=	208
1	„ sulphuric acid	=	40
			<hr/>
			248

To convert it into protochloride of mercury, it is mixed with 1 proportional of chloride of sodium, the chlorine of which combines with the mercury of the oxide of mercury in the protosulphate to form a protochloride, whilst its sodium becomes sulphate of soda, as shown in the following diagram, in which the ORIGINAL COMPOUNDS are printed in small capitals, the *products* in italics, and the component substances in common type: the equivalent numbers are affixed to the respective agents.

In washing calomel, sal-ammoniac is often used, in consequence of the extreme solubility which it confers on the perchloride of mercury: common salt answers equally well, and is cheaper; but it deserves notice, in relation to this part of the process, that calomel boiled with solution of sal-ammoniac, or of common salt, is resolved into metallic mercury and corrosive sublimate; the washings, therefore, where these salts are em-



ployed, should be with their cold solutions; but it is safer to wash with hot distilled water only, which when conjoined with perfect levigation, and tested as above directed, is very effective.

The form in which calomel sublimes depends much upon the dimensions and temperature of the subliming vessels. In small vessels it generally condenses in a crystalline cake, the interior surface of which is often covered with beautiful quadrangular prismatic crystals (BROOKE, *Ann. of Phil.*, ii. 427, 2nd series), transparent, and of a texture somewhat elastic or horny: in this state it acquires, by the necessary rubbing into powder, a decidedly yellow or buff tint, more or less deep according to the degree of trituration which it has undergone. If, on the contrary, the calomel be sublimed into a very capacious and cold receiver, it falls in a most impalpable and perfectly white powder, which only requires due elutriation to fit it for use; it then remains perfectly colourless. By a modification of the process, it may be suffered as it sublimes to fall into water, according to Mr. Jewell's patent.

The above circumstances, too, account for the various appearances under which calomel occasionally presents itself in commerce: it may be added, that the buff aspect of this substance indicates the absence of corrosive sublimate; though it by no means follows, as a consequence, that when snow-white it contains it. When the surface of massive sublimed calomel is scratched, it always exhibits a buff colour: it also becomes yellow when heated, but loses this tint as it again cools.

Calomel should be perfectly tasteless, inodorous, and insoluble in water. Dumas states it to be soluble in 12,000 parts of boiling water, and Graham says it is so insoluble, that when protonitrate of mercury is added to water containing a two hundred and fifty-thousandth part of hydrochloric acid, a sensible precipitate of calomel appears. I have found that, upon pouring hot distilled water upon pure calomel on a good filter, the liquor which passes is not affected by sulphuretted hydrogen. Its specific gravity is 7.17 (HASSENFRATZ), 6.5 (GRAHAM). At a heat somewhat below redness it rises in vapour, without previous fusion; but it fuses when subjected to heat under pressure. The density of its vapour is 8.2; or 119 in reference to hydrogen as unity. When scratched or broken in the dark, it phosphoresces. It is decomposed by the fixed alkalis and by ammonia, and protoxide of mercury is one of the results. Ammoniacal gas blackens calomel, but heat restores the original colour, and the calomel is unchanged. By strong hydrochloric acid it is resolved into mercury and corrosive sublimate, and by nitric acid into pernitrate of mercury and corrosive sublimate. Phosphorus, sulphur, and several of the metals decompose it. It consists of

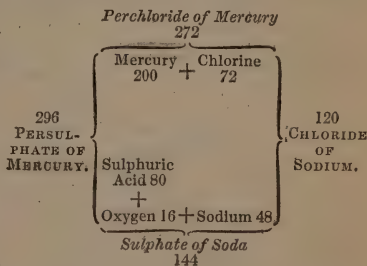
				Turner. Davy. Zabozda.
Mercury	1 . . .	200 . .	84.75 . .	85
Chlorine	1 . . .	36 . .	15.25 . .	15
Protochloride of mercury	1	236	100.00	100

Native Protochloride of Mercury, or *Mercurial Horn Ore*, has been found in Germany, France, and Spain, usually crystallized, and sometimes incrusting and massive: it is rare.

PERCHLORIDE OF MERCURY. BICHLORIDE OF MERCURY. OXYMURIATE OF MERCURY. CORROSIVE SUBLIMATE. ($hg + 2c$).—When mercury is heated in excess of chlorine, it burns with a pale flame, the gas is absorbed, and a white volatile substance rises, which is the *perchloride*. It may also be obtained by dissolving peroxide of mercury in hydrochloric acid, evaporating to dryness, redissolving in water, and crystallizing.

The ordinary process for making corrosive sublimate, consists in exposing a mixture of chloride of sodium and persulphate of mercury to heat in a proper subliming-vessel. The persulphate is formed by boiling 2 lbs. of mercury with 30 oz. of sulphuric acid to dryness; it is then rubbed to powder with 4 lbs. of chloride of sodium, and the mixture put into a large flask or into an earthen subliming-vessel, and exposed to a heat gradually raised to redness.

In this process the original substances are decomposed, *perchloride of mercury* sublimes, and *sulphate of soda* is the residue. The object, then, of the operation is, to obtain a compound of 1 proportional of mercury and 2 of chlorine, which is effected by the mutual decomposition of 1 proportional of persulphate of mercury, = 296, and 2 proportionals of chloride of sodium, $60 \times 2 = 120$, as shown in the annexed diagram:—

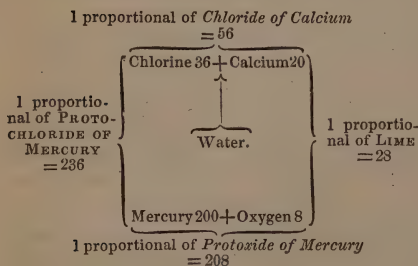
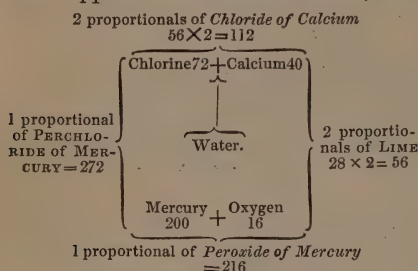


The *persulphate of mercury* is generally prepared upon the large scale, by heating the acid and metal in an iron pot, proper means being adopted to carry off the copious fumes of sulphurous acid arising from the decomposition of a portion of the sulphuric acid, during the peroxidizement of the mercury. The whole is then evaporated to dryness, and the subsequent sublimation is performed in glass, earthenware, or iron vessels, their form and arrangement being much dependent upon the quantity of materials employed.

Perchloride of mercury has an acrid nauseous taste, leaving a permanent metallic and astringent flavour upon the tongue. Its specific gravity is 5.2 (HASSENFRATZ,) 6.5 (GRAHAM). It is usually met with in the shops in the form of white semi-transparent and imperfectly-crystallized masses, or in powder. It frequently exhibits prismatic crystals upon the inner surfaces of the sublimed cakes. (BROOKE, *Ann. of Phil.*, 2nd series, vi. 285.) It is soluble in about 16 parts of cold, and 3 of hot water, and as the solution cools, it deposits quadrangular prismatic crystals: it is more copiously soluble in alcohol, 7 parts of which at 60° dissolve 3, and at its boiling point 6, of corrosive sublimate: it is also soluble in ether, which, at common temperatures, takes up about one-third its weight; and when ether is agitated with the aqueous solution it abstracts the perchloride from the water. When heated, it readily fuses, boils, and entirely sub-

limes in the form of a dense white vapour, powerfully affecting the nose and mouth. The density of its vapour is 9.420; 1 volume of it including 1 volume of mercury vapour and 1 volume of chlorine. It is insoluble in concentrated nitric and sulphuric acids. Hydrochloric acid of the specific gravity 1.158, at the temperature of 60°, dissolves about its own weight, and the solution, when cooled to about 40°, concretes into a mass of acicular crystals; there appear to be two or three of these definite *hydrochlorates of bichloride of mercury*; they are partially decomposed when added to great excess of water, and resolved into free hydrochloric acid and bichloride.

When solution of *perchloride of mercury* is decomposed by potassa, soda, or lime, a yellow precipitate is thrown down, which, when the alkali is in excess, is a hydrated *peroxide of mercury*. Such a mixture of a pint of lime-water with a drachm of corrosive sublimate was formerly much used as an application to venereal ulcers, under the name of *Aqua phagedænica*,



or *red lotion*. It is in fact a solution containing undecomposed corrosive sublimate and chloride of calcium, mixed with peroxide, or with oxichloride, of mercury. For the actual decomposition of 1 proportional of corrosive sublimate, 2 proportionals of lime are required, as shown in the annexed diagram, which also exhibits the theory of the decomposition.

When *protochloride of mercury*, or calomel, is similarly decomposed, a portion of *protoxide of mercury* is the result, as in the annexed diagram, and the mixture, which is known in pharmacy under the name of *black lotion*, is obtained.

Corrosive sublimate is either decomposed by, or combines with, the greater number of organic bodies; some of them convert it into calomel, by the abstraction of 1 atom of chlorine; others enter into more complicated combinations, some of which are remarkably permanent; the applications of it to the preservation of some anatomical preparations, and to the prevention of dry-rot, illustrate these actions, and will again be alluded to under organic bodies: hence also the efficacy of a mixture of white of egg and water, in preventing or mitigating the poisonous effects of corrosive sublimate in the stomach.

Perchloride of mercury consists of

				Davy.	Turner.
Mercury	1	200		73.53	
Chlorine	2	72		26.47	
Perchloride of mercury	1	272		100.00	

OXICHLORIDE OF MERCURY.—It has been stated that when a solution of corrosive sublimate is decomposed by excess of potassa or soda, a hydrated peroxide of mercury is thrown down; but if the mercurial salt remains in excess, the precipitate is then of a brown colour, and contains oxide and bichloride of mercury; when the alkaline carbonates are used, there are the same general results. "Chloride of mercury is not immediately precipitated by the bicarbonates of potassa and soda; hence that salt may be employed to detect the presence of a neutral alkaline carbonate in these bicarbonates. This oxichloride may also be formed by passing chlorine through a mixture of water and oxide of mercury. It may be obtained crystalline, and of a very dark colour, by mixing corrosive sublimate with chloride of lime, and boiling the liquid; or by treating a solution of corrosive sublimate with bicarbonate of potassa, and allowing the solution to stand in an open vessel, when carbonic acid gradually escapes, and the compound $(hg + 2c) + 4(hg + 2o)$ is deposited. This oxichloride is decomposed by a moderate heat; chloride of mercury sublimes, and the red oxide is left.

AMMONIO-CHLORIDES OF MERCURY.—Corrosive sublimate slowly absorbs about 4 per cent. of ammonia at common temperatures; when fused in an atmosphere of ammonia, the absorption is more rapid; the compound fuses, and consists of 1 atom of corrosive sublimate and 1 of ammonia. It boils at 590° , and may be distilled without decomposition; water decomposes it. (H. ROSE.) When chloride of mercury is dropped into a hot mixed solution of ammonia and sal-ammoniac, as long as the precipitate redissolves, crystals of an ammonio-chloride of mercury are formed, containing 1 atom of bichloride and 2 of ammonia. (KANE.) When a mixture of 1 part of sal-ammoniac and 5 of corrosive sublimate are dissolved in 6 of water, and the solution evaporated, a crystallized compound is obtained, formerly called *Sal alembroth*, or *salt of wisdom*. When this solution is diluted, and mixed with solution of potassa, a white powder falls, which was considered as identical with the precipitate obtained by decomposing solution of corrosive sublimate by ammonia, but which, according to Kane, is similar in composition to the crystalline salt just mentioned, namely $(hg + 2c) + 2(n + 3h)$.

White Precipitate.—This name was formerly given to the white powder which falls when ammonia is added to a solution of corrosive sublimate; it is the *Hydrargyri ammonio-chloridum* of pharmacy, and has generally been regarded as a compound of peroxide of mercury, bichloride of mercury, and ammonia. (See PHILLIPS, *Trans. Lond. Pharm.*, and HENNEL, *Quart. Journ.*, xviii. 297.) According to Kane, white precipitate is free from oxygen, and is a bichloride of mercury combined with an amide of mercury, or $(hg + 2c) + (hg + n + 2h)$. This compound is soluble in the acids, and is not altered by ammonia. When it is boiled in water, it is converted into a heavy yellow powder, which, according to Kane, is a double chloride and amide of mercury with oxide of mercury. According to Mitscherlich, white precipitate, when gradually and carefully heated, is decomposed, and part of it converted into a red matter, which contains 1 atom of perchloride of mercury united to a compound of 1 atom of nitrogen + 3 of mercury $(hg + 2c) + (n + 3hg)$. This red substance is decomposed, when heated above 680° , into corrosive

sublimate, mercury, and nitrogen; it is insoluble in water, and not altered by nitric acid or by the alkalis; it is decomposed when boiled in concentrated sulphuric or hydrochloric acid, and corrosive sublimate and ammonia are found in the solution. The nitruret of mercury has not been isolated. (*Poggendorf*, xxxix. 409.)

HYDRARGO-PERCHLORIDES OF POTASSIUM.—These and a number of similar double hydrargo-chlorides have been examined by Bonsdorff. (*Ann. de Ch. et Ph.*, xlv.) When 1 equivalent of bichloride of mercury and 1 of chloride of potassium are dissolved in water, and left to spontaneous evaporation, acicular amianthine crystals are formed, which contain 74·7 bichloride of mercury, 20·4 chloride of potassium, and 4·9 water, per cent., or 1 atom of each of the chlorides and 2 of water = $(hg + {}^2c) + (po + c) + {}^2q$. When 1 atom of bichloride of mercury and 2 of chloride of potassium are similarly combined, the resulting salt forms transparent rhomboidal crystals, which contain 62·0 of bichloride of mercury, 33·9 of chloride of potassium, and 4·1 of water, per cent.; they are, therefore, $(hg + {}^2c) + {}^2(po + c) + {}^2q$. There is a third of these compounds which is prepared by saturating cold water with chloride of potassium, heating the solution up to between 120° and 140°, and saturating it at that temperature with corrosive sublimate; the hot solution is filtered in a warm place, and it no sooner begins to cool than it concretes into a mass of white silky crystals; it may also be obtained in rhomboidal prisms; it contains 83·2 per cent. of bichloride of mercury, 11·3 of chloride of potassium, and 5·5 of water, numbers which are equivalent to 2 atoms of bichloride of mercury, 1 of chloride of potassium, and 4 of water, or $2(hg + {}^2c) + (po + c) + 4q$.

HYDRARGO-PERCHLORIDE OF SODIUM is obtained by adding to a cold saturated solution of common salt as much corrosive sublimate as it will dissolve, and, leaving the solution to spontaneous evaporation, it forms a mass of acicular crystals; or, if excess of common salt be present, regular six-sided prisms. This double chloride always contains

				Bonsdorff.
Bichloride of mercury	1	272	74·0	74·3
Chloride of sodium	1	60	16·3	15·9
Water	4	36	9·7	9·8
Hydrargo-perchloride of sodium	1	368	100·0	100·0

The hydrargo-bichlorides of calcium and of magnesium are as various as those of potassium; they are crystallizable, and the neutral salt is very deliquescent; those of barium, strontium, and lithium, resemble that of soda; those of manganese, iron, nickel, and cobalt, are neutral and isomorphous, forming rhomboidal prisms, which contain 4 atoms of water; that of zinc is very deliquescent; that of copper, permanent.

CHLORATES OF MERCURY.—Chloric acid dissolves both the oxides of mercury; the *protochlorate* has the appearance of a yellowish granular powder, sparingly soluble in hot water, and of a mercurial taste. The *perchlorate* forms white acicular crystals, having the acrid flavour of the perchloride, and soluble in 4 parts of water at 60°. (*VAUQUELIN*, *Ann. de Ch.*, xcv.)

PROTIODIDE OF MERCURY. (*hg + i*.)—This compound is obtained, 1. By triturating together 200 parts of mercury, and 126 parts of iodine, moistened with alcohol. 2. By adding iodide of potassium to a dilute solution of neutral protonitrate of mercury. 3. By digesting in boiling water 236 parts of protochloride of mercury with 166 of iodide of potassium. 4. By the mutual atomic decomposition of protacetate of mercury and iodide of potassium.

Protiodide of mercury is a dirty-green powder. When rapidly heated in a glass tube, it fuses, and sublimes unaltered: gently heated, or long exposed to light, it is resolved into mercury and periodide: it also undergoes the same decomposition by the action of hydriodic acid on the basic iodides, and, when aided by heat, by hydrochloric acid and the basic chlorides. It consists of

Mercury	1	200	61.5
Iodine	1	126	38.5
Protiodide of mercury	1	326	100.0

SESQUIODIDE OF MERCURY. YELLOW IODIDE OF MERCURY.—When iodide of potassium is poured into an acid solution of protonitrate of mercury, the resulting precipitate is, under careful management, yellow, and consists chiefly of sesquiodide; but if too much acid be used, it is of a reddish tinge from the presence of periodide, which, however, may be removed by digesting the precipitate in alcohol. The sesquiodide of mercury is more certainly obtained by precipitating the protonitrate by a sesquiodide of potassium, made by dissolving half an equivalent of iodine with 1 equivalent of iodide of potassium: it then falls in the form of a yellow precipitate, which when washed with alcohol is free from periodide. This sesquiodide is a yellow powder, which by the action of dilute nitric acid is converted into periodide, so that the precipitate which falls when iodide of potassium is added to protonitrate of mercury, varies in composition with the state of the mercurial salt: if neutral, the green protiodide falls; if slightly acid, the yellow sesquiodide; if very acid, the red periodide. The yellow compound contains

Mercury	1	200	51.5	Boullay.	51.9
Iodine	1½	189	48.5		48.1
Sesquiodide of mercury	1	389	100.0		100.0

PERIODIDE OF MERCURY. BINIODIDE OF MERCURY (*hg + 2i*) is of a bright scarlet colour, easily fusible, and then assumes a yellow colour: it sublimes in rhomboidal scales, at first yellow, but becoming red on cooling or when subjected to friction. The density of its vapour is 15.680. Acids and alcohol dissolve it by the aid of heat, and as the solutions cool it separates in more or less perfect crystals; it dissolves also in solutions of the mercurial salts and of iodide of potassium. It is almost insoluble in water. It is precipitated by sulphuric acid from its solution in caustic potassa. It absorbs about 6 per cent. of ammonia and loses its red colour: exposed to air the ammonia escapes and the red colour returns. This iodide is obtained by triturating 2 equivalents of iodine with 1 of mercury, or by precipitating a perntrate of mercury with a proper quantity of iodide of potassium: it is generally made by adding a solution of

iodide of potassium to one of corrosive sublimate: when the iodide is gradually dropped into the mercurial solution, a red compound of chloride and iodide of mercury is first formed, which presently redissolves; on adding more of the iodide a pale flesh-coloured precipitate falls, which is an insoluble iodochloride; a further addition of iodide of potassium produces a bright scarlet precipitate, which is periodide of mercury; lastly, excess of iodide of potassium redissolves the periodide, and a soluble hydrargio-iodide of potassium is formed. Biniodide of mercury consists of

Mercury	1	200	44.4
Iodine	2	252	55.6
<hr/>			
Periodide of mercury	1	452	100.0

HYDRIODATES OF PERIODIDE OF MERCURY are formed by the periodide in various equivalent proportions dissolved in hydriodic acid: a hydriodate and a binhydriodate may be thus formed, and obtained in yellow acicular crystals by careful evaporation in vacuo; they are decomposed by water, and if left too long under evaporation a portion of their component acid goes off.

HYDRARGO-PERIODIDES. — Biniodide of mercury unites with other iodides, and forms a class of double salts which have been examined by Boullay and by Bonsdorff (*Ann. de Ch. et Ph.*, xxxiv. and xlv.): it also combines with certain chlorides, as above mentioned in regard to the chloride of mercury; thus, when biniodide of mercury is digested in a hot solution of bichloride of mercury, two double salts are deposited as the solution cools; one in the form of a yellow powder $(hg + 2i) + (hg + 2c)$, and the other in white dendritic crystals, which is $(hg + 2i) + 2(hg + 2c)$.

HYDRARGO-PERIODIDE OF POTASSIUM forms yellow acicular deliquescent crystals, when a cold solution of iodide of potassium is saturated with periodide of mercury, and left to spontaneous evaporation in a vacuum with quick-lime: they are soluble in alcohol and ether, and contain 1 atom of iodide of potassium + 1 of biniodide of mercury + 3 of water; their equivalent being 645. When this salt is dissolved in a large quantity of water, half of its component biniodide of mercury separates, and on evaporating the solution a yellow residue is obtained, containing 2 atoms of iodide of potassium + 1 of biniodide of mercury.

There are analogous *hydrargo-periodides of calcium, magnesium, barium, strontium, iron, zinc, &c.*

IODATE OF MERCURY. — Iodate of potassa occasions a white insoluble precipitate in the protonitrate of mercury, but not in the pernitrate; hence the iodate of the peroxide appears to be a soluble salt.

BROMIDES OF MERCURY. — Bromide of potassium occasions a white curdy precipitate in the protonitrate of mercury, which is a *protobromide of mercury*: the *perbromide* may be obtained by the direct action of bromine on mercury, or on peroxide of mercury; it is a white crystallizable compound, fusible, volatile, and soluble in water and in alcohol. It forms double salts (*hydrargo-bromides*) with the bromides of the alkaline bases. It absorbs ammonia when heated in that gas, but not at common temperatures.

The *Bromates of Mercury* have not been examined.

FLUORIDES OF MERCURY.—Hydrofluoric acid occasions no precipitate in the protonitrate of mercury, and when the mixture is evaporated, the acid escapes, and leaves the mercurial salt unchanged. When hydrofluoric acid is poured upon peroxide of mercury, it acquires an orange-colour, and is dissolved upon the addition of water. The solution furnishes yellow prismatic crystals, which, by the action of hot water, are resolved into a soluble and insoluble compound. (BERZELIUS.)

MERCURY AND NITRIC ACID.—Nitric acid is rapidly decomposed by mercury: nitrous acid, and nitric oxide gases are evolved, and either a *protonitrate* or a *pernitrate* of mercury is obtained, according to the mode in which the solution is performed and the state of dilution of the acid.

PROTONITRATE OF MERCURY ($hg + o + n'$) is obtained by dissolving the metal in cold nitric acid: the solution deposits transparent crystals, which appear to be modified octoëdra, or, according to Thomson, four-sided prisms. They are soluble without decomposition in a small proportion of cold water, and the solution affords black precipitates upon the addition of excess of the alkalis. Small quantities of the caustic alkalis dropped into this solution, occasion yellowish and gray precipitates, which appear to be mixtures of the oxide and subnitrate. The *crystallized protonitrate* contains, according to Thomson (*First Principles*), and Mitscherlich (*Ann. de Ch. et Ph.*, xxv. 241), 2 atoms of water: its composition therefore is

Protoxide of mercury	1	208	74.3
Nitric acid	1	54	19.3
Water	2	18	6.4
<hr/>					
Crystals of protonitrate of mercury	1		280		100.0

As a test, a solution of protonitrate of mercury is useful in the following cases: with sulphuretted hydrogen it yields a *black* precipitate, with hydriodic salts *greenish-yellow*, with hydrochloric acid and salts *white*, with ammonia *black*, with fixed alkalis *gray*, with chromic acid *red*, with arsenious acid *white* or *straw-colour*: it discolours an extremely dilute solution of gold, rendering it *dark-brown*, and of platinum *yellowish-brown*, or if very dilute, *yellow*. It throws down white flakes from albuminous solutions. The nitric solutions of mercury, when concentrated, tinge the cuticle of a dingy purple.

SUBPROTONITRATE OF MERCURY.—When excess of mercury is digested in cold nitric acid diluted with 3 or 4 parts of water, or when protoxide of mercury is digested in a solution of the neutral protonitrate, white prismatic crystals are deposited, soluble in a small quantity of water, but decomposed by a large quantity, when a white powder is deposited which becomes yellow if washed with water. The crystals contain 1 atom of nitric acid, $1\frac{1}{2}$ of protoxide of mercury, and $1\frac{1}{2}$ of water (MITSCHERLICH); and the yellow pulverulent salt, 1 atom of nitric acid, 2 of protoxide of mercury, and 1 of water. (KANE.)

When the preceding nitrates are decomposed by a dilute solution of ammonia, not in excess, a dark-gray precipitate falls, which when collected

and well washed was formerly known as *Hahnemann's Soluble Mercury*: it is a compound of 1 atom of nitric acid, 2 of protoxide of mercury, and 1 of ammonia. When mercury is boiled in an aqueous solution of the protonitrate till the liquid is of a dark-yellow colour, it yields, on evaporation, a difficultly-soluble yellow salt which is a hyponitrite (nitrite?) of mercury. (MITSCHERLICH.)

PERNITRATE OF MERCURY.—There is no neutral pernitrate of mercury, that is, in which 1 atom of the peroxide is combined with 2 of nitric acid, which is susceptible of being crystallized; but such a compound probably exists in solution, when 1 atom of corrosive sublimate is decomposed by 2 of nitrate of oxide of silver: for $(hg + 2c) + 2(ag + o + n')$ become $2(ag + c) + (hg + 2o + n')$, or when 1 atom of peroxide of mercury is dissolved in 2 of nitric acid; but when such a solution is evaporated, or when mercury is boiled in nitric acid till a drop of the liquid occasions no precipitate when added to solution of chloride of sodium, and then set aside to crystallize, a salt is obtained in small prisms which consists of

				Mitscherlich.
Peroxide of mercury	1 . . .	216 . .	75.00 . .	75.9
Nitric acid	1 . . .	54 . .	18.75 . .	18.9
Water	2 . . .	18 . .	6.25 . .	5.2
Pernitrate of mercury crystallized	1	288	100.00	100.0

SUPERNITRATE OF MERCURY is the result of the decomposition of the preceding salt by tepid water; it falls in the form of a yellow powder, which consists of $1\frac{1}{2}$ atoms of peroxide, 1 of nitric acid, and 1 of water: when boiled in water it becomes more basic, and probably forms a definite compound of 3 atoms of peroxide, 1 of acid, and 1 of water. (KANE.)

Action of Ammonia on the Pernitrates of Mercury.—When these salts are decomposed by ammonia several complicated results ensue, which have been studied by Mitscherlich, Soubeiran, and Kane. When a solution of pernitrate of mercury is decomposed by weak solution of ammonia a white precipitate ensues, which when washed in cold water contains $1\frac{1}{2}$ atoms of peroxide of mercury, 1 of ammonia, and 1 of nitric acid (MITSCHERLICH): when treated by boiling water it is heavier and more granular, and then consists of a subnitrate of mercury, $\frac{1}{2}(hg + 2o) + n'$, combined with an amide of mercury $(hg + 2n + 4h)$. (KANE.) When the preceding salts are boiled with nitrate of ammonia and excess of ammonia, the resulting solution deposits yellow crystals on cooling, the constituents of which are 1 atom of peroxide, 1 of ammonia, and 1 of nitric acid. (SOUBEIRAN.) When this salt is boiled in a strong solution of nitrate of ammonia the solution deposits, on cooling, brilliant acicular crystals, which are resolved by water into Soubeiran's subsalt and nitrate of ammonia: the crystals contain 3 atoms of nitrate of ammonia, and 3 of water (or 3 atoms of nitrate of oxide of ammonium), combined with 2 atoms of peroxide of mercury. (*Ann. de Ch. et Ph.*, LXXII. 225. *Trans. Royal Irish Acad.*, xix.)

NITRICO-OXIDE OF MERCURY.—When the nitrates of mercury are exposed to heat gradually raised to dull redness, nitric and nitrous acid is

given off, and a red substance remains, consisting of peroxide of mercury with a small portion of adhering nitrate. This is used in pharmacy as an escharotic, and is called in the *London Pharmacopœia*, *hydrargyri nitrico-oxidum*. It is difficult in this process so to apply the heat as to expel the acid, without at the same time evolving oxygen from the remaining oxide and evaporating part of the mercury. We find, therefore, traces of nitric acid generally remaining in the compound. The nitrate requires to be constantly stirred during the process, which is usually performed in a cast-iron pot; the operator will find it advantageous to prepare the solution and partly to evaporate it in a retort with an annexed receiver containing a little water, by which, if any quantity of materials is employed, he will save a part of the acid. The product, when well prepared, is of a brilliant red colour, with a shade of orange; when not in very fine powder it has a glistening scaly appearance; at a red heat it is decomposed and entirely dissipated, provided it be not adulterated, as it sometimes is, with red-lead: it has an acrid taste, is very sparingly soluble in water, and readily soluble without effervescence in nitric acid. According to Gay Lussac, the appearance of this preparation depends on the state of the nitrate previous to decomposition; if in fine powder, the resulting oxide is orange-coloured and pulverulent; the larger crystals furnish a deeper-coloured oxide, and the small crystals yield that which is preferred in commerce; the pernitrate furnishes a finer-coloured product than the protonitrate. In consequence of subpernitrate of mercury remaining in this preparation, it should not be used in medicine as a substitute for pure peroxide of mercury. When washed with and triturated in a dilute solution of potassa,edulcorated with distilled water, and carefully dried, it may be regarded as nearly pure peroxide of mercury. In this state it is called *Arcanum corallinum* in some of the older *Pharmacopœiæ*.

MERCURY AND SULPHUR. PROTOSULPHURET OF MERCURY. (*hg + s.*) — When 1 part of mercury is triturated for some time with 3 of sulphur, a black tasteless compound is obtained, which was called in old pharmacy *Ethiops mineral*; it is the *Hydrargyri sulphuretum nigrum* of the *Pharmacopœia*, and is often regarded as a definite sulphuret; but when boiled in solution of potassa, sulphur is taken up, and bisulphuret of mercury remains, so that it is probably a mixture of sulphur and of the bisulphuret. According to Taddei, an *Ethiops mineral* may be quickly formed by the following process. (*Gior. di Fisica*, iv. 12.) Put 1 part of sulphuret of potassa with 3 of mercury into a mortar, and triturate with a little water, until the whole forms a homogeneous black paste; then add flowers of sulphur equal in weight to the mercury, and mix the whole: wash with repeated affusions of water, till the alkaline sulphuret is removed, and carefully dry the remaining *Ethiops*.

When sulphuretted hydrogen is passed through a dilute solution of protonitrate of mercury, or through a mixture of very finely divided calomel and water, a black powder is thrown down, which is a true protosulphuret. When it is boiled with nitric acid, it is converted into a sulphate of mercury: heated to redness, metallic mercury escapes, and bisulphuret sublimes. By long exposure to light it is said to be resolved into mercury and bisulphuret. It consists, according to Guibourt (*Ann.*

de Ch. et Ph., i.), of 100 mercury + 8.2 sulphur, numbers which correspond to

Mercury	1 . . .	200 . . .	92.6
Sulphur	1 . . .	16 . . .	7.4
<hr/>			
Protosulphuret of mercury	1	216	100.0

BISULPHURET OF MERCURY. VERMILION. CINNABAR. ($hg + 2s$).—In the manufacture of cinnabar, 6 parts of mercury are mixed in an iron pot with 1 of sulphur, and made to combine by a moderate heat, and constant stirring: this compound is then transferred to a glass subliming-vessel, (on a small scale, a Florence flask answers perfectly,) and heated to redness in a sand-bath; a quantity of mercury and of sulphur evaporate, and a sublimate forms, which is removed, and rubbed or levigated into a very fine powder. If mercury and sulphur be heated together in large quantities, the action is so intense at the moment of their combination as to occasion a slight explosion and flame; sulphuretted hydrogen is also evolved. The details of the process for the manufacture of cinnabar are given by Dumas (*Chimie app. aux Arts*); but, however finely it is triturated, it never acquires the brilliant tint of the sulphuret prepared by humid processes, or of that which is imported from China.

When solution of corrosive sublimate is decomposed by the action of excess of sulphuretted hydrogen, the precipitate which falls is a bisulphuret of mercury; but it is perfectly black until sublimed, when it forms a steel-gray sublimate, which, reduced to a fine powder, acquires its red tint.

Kirchoff was the first who pointed out a mode of obtaining vermilion by the process of triturating mercury and sulphur in a solution of potassa. (NICHOLSON'S *Journal*, 4to. ii.) A black compound is first formed, and the mixture is then heated to 130° , and retained for several hours at about that temperature, when it gradually acquires a brown and then a red tint; when this is sufficiently brilliant the liquid is decanted, and the product washed and dried. Liebig obtains vermilion by digesting recently prepared *white precipitate* (see page 937) in a sulphuret of ammonium, obtained by saturating hydrosulphuret of ammonia with sulphur: the black sulphuret is first produced, which afterwards acquires the desired red colour; its tint is improved by digestion at a gentle heat in a strong solution of potassa.

Cinnabar is not altered by exposure to air or moisture; when heated to dull redness in an open vessel, the sulphur forms sulphurous acid, and the mercury escapes in vapour. It is decomposed by distillation with fixed alkalis, lime, and baryta, and by several of the metals. When adulterated with red-lead or with colcothar, it is not entirely volatile. It is insoluble in nitric and hydrochloric acids, but nitrohydrochloric acid acts upon, and decomposes it, even in the cold. Boiled in sulphuric acid, sulphurous acid is evolved, and a sulphate of mercury formed. It consists of

				Seftstrom.	Guibourt.	Seguier.	Proust.
Mercury	1 .	200 .	86.2 .	86.29 .	86.21 .	85.5 .	85 .
Sulphur	2 .	32 .	13.8 .	13.71 .	13.79 .	14.5 .	15 .
<hr/>							
Bisulphuret of mercury	1	232	100.0	100.00	100.00	100.0	100

Native Cinnabar is the principal ore of mercury: it occurs massive, and crystallized in six-sided prisms, rhombs, and octoëdra. It is of various colours, sometimes appearing steel-gray, at others bright-red. It occurs in Hungary, France, and Spain, in Europe; in Siberia and Japan, in Asia; and in considerable quantities in South America. The mines of Almaden, and of New Spain, are the most productive, and furnish fine cabinet specimens. Native mercury, and native amalgam of silver, sometimes accompany it.

CHLOROSULPHURET OF MERCURY. $(hg + 2c) + 2(hg + 2s)$.—When sulphuretted hydrogen gas is passed through a solution of corrosive sublimate a white precipitate is first formed, which is long in subsiding, and readily passes through filtering paper: if the action of the gas be continued, this white compound blackens and becomes bisulphuret of mercury. The same white compound is formed by digesting precipitated bisulphuret of mercury in a solution of corrosive sublimate. It may be washed, and dried without decomposition: when heated, corrosive sublimate rises first, and afterwards bisulphuret of mercury: it is insoluble in the greater number of acids, but nitrohydrochloric acid decomposes it; chlorine converts it into chloride of sulphur and perchloride of mercury: the alkalis blacken it, and forming chlorides of their bases separate sulphur and peroxide of mercury. It consists of

Perchloride of mercury . . .	1	. . .	272	. . .	36.9
Bisulphuret of mercury . . .	2	. . .	464	. . .	63.1
<hr/>					
Chlorosulphuret of mercury	1		736		100.0

IODOSULPHURET OF MERCURY $(hg + 2i) + 2(hg + 2s)$ is an analogous compound to the preceding, obtained by the action of sulphuretted hydrogen upon biniodide of mercury. It is of a yellow colour.

BROMOSULPHURET OF MERCURY $(hg + 2b) + 2(hg + 2s)$ is yellowish-white, and resolved by heat into bromide of mercury, which is most volatile, and sulphuret, which subsequently sublimes.

FLUOSULPHURET OF MERCURY. $(hg + 2f) + 2(hg + 2s)$.—When a solution of peroxide of mercury in hydrofluoric acid is subjected to the action of sulphuretted hydrogen, a white precipitate is obtained, which is characteristically distinguished from the preceding combinations by its being decomposed by boiling water into sulphuret of mercury and perfluoride of mercury. When heated with sulphuric acid, hydrofluoric acid is disengaged.

HYPOSULPHITES OF MERCURY.—When a solution of a hyposulphite is poured into a very dilute solution of protonitrate of mercury it occasions a black precipitate, which, however, is probably not a true hyposulphite. The nature of these compounds has not been satisfactorily ascertained.

SULPHITES OF MERCURY AND HYPOSULPHATES OF MERCURY have not been examined.

PROTOSULPHATE OF MERCURY. ($hg + o + s'$).—When 1 part of mercury is digested in a moderate heat with $1\frac{1}{2}$ of sulphuric acid, sulphurous acid gas is evolved, and a white deliquescent mass is obtained, which, washed with cold water, affords a very difficultly-soluble white salt, which is a *protosulphate of mercury*. The same salt is thrown down, when sulphuric acid or sulphate of soda is added to a solution of proto-nitrate of mercury: it is also formed by triturating equivalent proportions of mercury and persulphate, and heating the mixture, as in the process for making calomel (p. 933). Protosulphate of mercury requires 500 parts of cold and 300 of boiling water for its solution: it crystallizes in prisms. According to Fourcroy, it is soluble in dilute sulphuric acid, and thus forms a crystallizable *supersulphate*. Its solution in boiling water is decomposed by the fixed alkalis, which at first throw down a subsalt, and when added in excess, separate the black protoxide. This salt, when anhydrous, consists of

Protoxide of mercury	. 1	. . 208	. . 83.9
Sulphuric acid	. . 1	. . 40	. . 16.1
Protosulphate of mercury	1	248	100.0

When protosulphate of mercury is decomposed by ammonia, it yields a dark-gray powder, which apparently contains ammonia.

PERSULPHATE OF MERCURY. ($hg + 2o + 2s'$).—If 5 parts of sulphuric acid be boiled down to dryness with 4 of mercury, a white crystalline mass of *persulphate of mercury* is obtained. This salt cannot exist in solution in the neutral state, for water resolves it into a soluble *supersalt* and an insoluble *subsalt*. The soluble portion may be obtained by evaporation in the form of deliquescent acicular crystals. The subsalt, when triturated with boiling water, acquires a yellow colour, and was formerly called *turpeth mineral*, from a similarity, in its medical effects, to the roots of the *Convolvulus turpethum*: it is dangerously cathartic and emetic. It is not absolutely insoluble in water, but requires 2000 parts of cold and 300 boiling water for the purpose. It contains $1\frac{1}{2}$ atoms of peroxide of mercury + 1 of sulphuric acid. Ammonia converts the sulphates of mercury into a heavy powder, similar in composition to that which results from the decomposition of white precipitate: it is a compound of turpeth with amide of mercury. (KANE.) The anhydrous persulphate of mercury consists of

Peroxide of mercury	. 1	. . 216	. . 73
Sulphuric acid	. . 2	. . 80	. . 27
Persulphate of mercury	1	296	100

PHOSPHURET OF MERCURY may be formed by heating phosphorus with oxide of mercury, or with the protosulphuret; or by passing the vapour of phosphorus over calomel; or phosphuretted hydrogen through a solution of protonitrate of mercury. It varies in appearance, and according to the method of its production its colour is either brown or black. When obtained by the action of phosphuretted hydrogen upon mercurial solutions, it almost always contains portions of the salt employed; and by acting upon solutions of persalts of mercury by phosphuretted hydrogen,

the first precipitate is white or yellow, and is a compound of phosphuret of mercury and the salt of the peroxide. These combinations have been described by H. Rose. (*Ann. de Ch. et Ph.*, LXVI. 366.)

Neither the HYPOPHOSPHITE nor PHOSPHITE OF MERCURY have been examined.

PHOSPHATES OF MERCURY.—When phosphate of soda is dropped into *protonitrate* of mercury, a white crystalline precipitate falls, which is *protophosphate of mercury*. It is insoluble in water and in excess of phosphoric acid, and when intensely heated is decomposed, and leaves phosphoric acid. *Perphosphate of mercury* is thrown down from the *pernitrate* by the addition of phosphate of soda: it resembles the *protophosphate* in appearance, but it dissolves in excess of phosphoric acid.

SELENIURET OF MERCURY is a tin-coloured substance, which sublimes in shining scales at a temperature below its point of fusion.

BISELENIURET OF MERCURY is obtained as a gray crystalline mass, by fusing the seleniuret with selenium.

Native Seleniuret of Mercury has been found in combination with seleniuret of lead.

CARBONATES OF MERCURY.—When solution of carbonate of potassa is dropped into *protonitrate* of mercury, a yellowish-white *protocarbonate of mercury* is thrown down; it becomes gray, and evolves carbonic acid, when boiled in water. It is soluble in excess of the alkaline carbonate, and in aqueous solution of carbonic acid. The *percarbonate of mercury* is of a reddish colour, and very easy of decomposition.

MERCURY AND CYANOGEN. BICYANURET OF MERCURY. ($hg + 2cy.$)
—There is no compound of 1 atom of mercury and 1 of cyanogen (in our equivalents), and which would correspond with the protoxide and protochloride. When a protosalt of mercury is added to hydrocyanic acid, metallic mercury is set free, and a bicyanuret is formed. There are several processes in common use for the preparation of this bicyanuret: 1. By boiling 1 part of finely-powdered peroxide of mercury with 2 of pure Prussian blue in 8 parts of water, a solution is obtained, which, if filtered while hot, deposits, on cooling, crystals of the bicyanuret. 2. When peroxide of mercury is brought into the contact of the vapour of hydrocyanic acid they act intensely upon each other, and water and bicyanuret of mercury are immediately formed. The attraction of mercury for cyanogen is so strong, that peroxide of mercury decomposes nearly all the metallic cyanurets, not excepting that of potassium; but the salts of palladium decompose the cyanuret of mercury. 3. Peroxide of mercury may be digested in aqueous hydrocyanic acid; the oxide, in very fine powder, may be agitated and left in contact with the acid till its odour is lost; more of the acid is then added to the decanted liquid, and on evaporation the bicyanuret is obtained. Graham recommends Winkler's process: 15 parts of ferrocyanuret of potassium, 13 of sulphuric acid, and 100 of water, are distilled by a moderate heat nearly to dryness, the vapour being condensed into 30 parts of water: a portion of the resulting

acid is put aside, and the remainder mixed with 16 parts of finely-powdered peroxide of mercury, and agitated till the odour of the acid disappears: the solution is then poured off from the undissolved oxide, and the reserved portion of the acid added to it; this is done to saturate a portion of oxide of mercury which the cyanuret dissolves in excess: 12 parts of cyanuret of mercury are then obtained by evaporation. 4. To a solution of 2 parts of ferrocyanuret of potassium in 15 of boiling water, add 3 parts of dry persulphate of mercury; boil for 15 minutes, and filter off the clear liquid whilst hot: as it cools, bicianuret of mercury crystallizes, which must be purified by a second crystallization: evaporate the mother liquid to dryness and digest the residue in alcohol, which takes up a further quantity of bicianuret. In this process there is a mutual decomposition of 2 equivalents of cyanuret of potassium (of the ferrocyanuret) and 1 of persulphate of mercury, into bicianuret of mercury and sulphate of potassa; cyanuret of iron is at the same time precipitated. (LIEBIG.)

Bicyanuret of mercury forms anhydrous prismatic crystals, their primary form being a right square prism (BROOKE, *Ann. of Phil.*, 2nd series, vi. 42), nearly colourless, or of a pale buff colour, at first transparent, permanent in the air, poisonous, and of a nauseous metallic taste: they dissolve in 8 parts of water at 60°, but in less boiling water, and are soluble in alcohol.

This salt is decomposed by heat, as in the process for obtaining cyanogen, and a black matter remains in the retort, which, according to Johnston, is paracyanogen. If distilled with hydrochloric acid, hydrocyanic acid and chloride of mercury are formed: it also is decomposed by hydriodic acid and by sulphuretted hydrogen, an iodide and a sulphuret of mercury, and hydrocyanic acid, being formed. Nitric acid dissolves it without decomposition. It is decomposed when heated with sulphuric acid. The alkalis do not act upon this cyanuret. It slowly absorbs a small portion of ammoniacal gas. Bicyanuret of mercury consists of

				Gay Lussac.	Porret.
Mercury	1	200	79.37	79.91	79.08
Cyanogen	2	52	20.63	20.09	
Bicyanuret of mercury	1	252	100.00	100.00	

OXICYANURET OF MERCURY.—When a solution of bicianuret is boiled with excess of peroxide of mercury, a compound is obtained in acicular crystals, on evaporation, which is more soluble than the bicianuret, and has an alkaline reaction on vegetable colours. The formation of this and the succeeding compound must, as already stated, be avoided in preparing bicianuret of mercury. This salt is a tribasic cyanuret of peroxide of mercury ($hg + 2cy + 3(hg + 2o)$). (KUHN.) When strong aqueous hydrocyanic acid is agitated with excess of peroxide of mercury, a white salt is formed, which may be separated by boiling water, and which crystallizes on cooling in transparent four-sided acicular prisms. When gently heated it blackens and explodes: it is a compound of 1 atom of bicianuret with 1 of peroxide of mercury. (JOHNSTON, *Phil. Trans.*, 1839.)

HYDRARGO-CYANURETS.—These compounds are formed by digesting bichanuret of mercury in solutions of cyanuret of potassium, sodium, calcium, barium, &c. *The hydrargo-cyanuret of potassium* yields octoëdral crystals, which contain 1 atom of cyanuret of mercury + 2 of the alkaline cyanuret.

Bichanuret of mercury also forms compounds with chlorides, iodides, bromides, and with several oxisalts. When bichanuret of mercury and iodide of potassium are mixed in solution, pearly crystals fall, which, when redissolved, yield large thin brilliant plates, requiring 16 parts of water at 60° for their solution. They are decomposed by heat, and leave a residue of iodide of potassium and charcoal. (*Ann. de Ch. et Ph.*, xix. 220.)

FULMINATING MERCURY. FULMINE OF MERCURY. $2(hg + o) + (2cy + 2o)$.—This compound was discovered by Mr. Howard. (*Phil. Trans.*, 1800, p. 214.) It is prepared by dissolving 100 grains of mercury in a measured ounce and a half of nitric acid, aided by heat. This solution is to be poured, when cool, into two measured ounces of alcohol in a glass basin, and gently warmed: it soon begins to effervesce and evolve ethereal vapour, and if the action is too violent, it must be quelled by cooling the vessel, or by the addition of a little cold alcohol. During this action a yellow-gray precipitate falls, which is to be immediately separated by decantation and filtration, washed with small quantities of distilled water, and carefully dried at a heat not exceeding 100°. The above quantity of mercury yields about 120 grains of the powder when the operation has been most successful. If the product is mixed with metallic mercury, it may be purified by solution in boiling water, from which it is deposited in silky acicular crystals. (See p. 564.)

This compound, when heated to about 300°, explodes with a bright flame: it also detonates by friction, by the electric spark, and by contact of concentrated sulphuric and nitric acids: the gases evolved by its explosion are carbonic acid, nitrogen, and the vapour of mercury. Liebig and Gay Lussac have furnished some curious facts towards the history of this compound (*Ann. de Ch. et Ph.*, xxiv. and xxv.): it consists of

Protoxide of mercury	2	.	416	.	86.0		2	.	416	.	86
Cyanogen	2	.	52	.	10.7	Fulminic acid }	1	.	58	.	14
Oxygen	2	.	16	.	3.3		1	.	58	.	14
Fulminate of mercury	1		484		100.0		1		484		100

FERROCYANURET OF MERCURY.—When any solution of a mercurial salt is mixed with ferrocyanuret of potassium, a white precipitate falls, which decomposes spontaneously into cyanuret of iron, and cyanuret of mercury; the latter is dissolved, and if a protosalt has been used, metallic mercury is also separated: these changes are accelerated by heat.

SULPHOCYANURET OF MERCURY.—When sulphocyanuret of potassium is mixed with protonitrate of mercury, a white precipitate falls. See Wöhler (*GILB. Annalen*, lxix.), and Berzelius (*Lehrbuch*), in reference to these compounds.

BORATES OF MERCURY.—When solution of protonitrate of mercury and of borate of soda are mixed and evaporated, small shining crystals of *protoborate of mercury* are obtained. Boracic acid occasions no precipitates in solution of pernitrate of mercury. The *Perborate of Mercury* has not been examined.

ARSENATE OF MERCURY.—Arsenic acid occasions a pale-yellow precipitate in solution of protonitrate of mercury: arseniate of soda throws down a gray powder from the same solution, which, when dried, loses no weight on the sand bath, and is therefore probably anhydrous. Arsenic acid forms a yellowish-white precipitate in solution of the pernitrate, and arseniate of soda throws down the same from a solution of corrosive sublimate. When arsenic acid is heated over mercury, arsenious acid is sublimed, and the same yellow arseniate formed. (THOMSON.) The arseniates of mercury are soluble in excess of arsenic acid: they have not been analyzed. Arsenious acid produces white precipitates in both solutions. These precipitates are soluble in hydrochloric acid.

MOLYBDATE OF MERCURY.—Molybdic acid occasions a yellow precipitate in solution of protonitrate of mercury, easily soluble in nitric acid. Molybdate of potassa also throws down a yellow precipitate from the protonitrate, which is very sparingly soluble in water, and decomposed by nitric acid.

CHROMATE OF MERCURY.—Chromate of potassa throws down an orange-red precipitate from the solution of protonitrate of mercury: its colour is brightest when the solution is acid, but in that case a portion of chromate remains dissolved. This salt is an excellent source of oxide of chromium, which remains when it is heated so as to expel mercury and oxygen.

ALLOYS OF MERCURY. AMALGAMS.—Mercury combines with most of the other metals, and forms a class of compounds generally called *amalgams*. Many of these are definite and crystallizable compounds, and may be separated, by gentle pressure, from the mercury in which such definite compound is suspended or dissolved. They are generally brittle or soft. 1 part of *potassium* with 70 of mercury produce a hard brittle compound. If mercury be added to the liquid alloy of *potassium* and *sodium*, an instant solidification ensues, and heat enough to inflame the latter metals is evolved. *Iron* and mercury may be combined by triturating together clean iron filings and zinc-amalgam, and adding a solution of perchloride of iron: by rubbing and heating this mixture, the iron and mercury form a bright amalgam. (ARTHUR AIKIN.) Under common circumstances, iron resists the action of mercury so perfectly, that the latter metal is usually kept in iron bottles; and mercurial troughs and barometer cisterns are made of the same metal. The use of an amalgam of *zinc* has already been adverted to for the excitation of electrical machines. 8 parts of mercury and 1 of *zinc* form a white brittle compound: 5 of mercury and 2 of *zinc* form a crystallizable amalgam. Amalgam of *tin* is easily formed by triturating the metals together, or fusing them by a gentle heat: its density exceeds the mean of its components: it is largely used for silvering looking-glasses. This beautiful

process is performed as follows:—A single and perfect sheet of tinfoil, of proper thickness, and somewhat larger than the plate of glass, is spread upon a perfectly plane table of slate or stone: mercury is then poured upon it, and rubbed upon its surface by a hare's foot, or a ball of flannel or cotton, so as to form a clean and bright amalgam; upon this, excess of mercury is poured, till the metal has a tendency to run off: the plate of glass, previously made quite clean, is then brought horizontally towards the table, and its edge so adjusted, as by gradually and steadily sliding it forward, to displace some of the excess of mercury, and float the plate as it were over the amalgam, the dross upon its surface being pushed onwards by the edge of the glass, so that the mercury appears beneath it with a perfectly uniform, clean, and brilliant reflecting surface: a number of square-weights, of 10 or 12 lbs. each, are now placed side by side upon the surface of the plate, so as entirely to cover it, and press it down upon the amalgamated surface of the tin; in this way the excess of mercury is partly squeezed out, and the amalgam is made to adhere firmly to the glass. The mercury, as it runs off, is received into a channel on the side of the table, which is slightly inclined to facilitate the drainage, and in about 48 hours the weights are taken off and the plate is carefully lifted from the table and set nearly upright, by which the adhering mercury gradually drains off, and the solid crystalline amalgam remains, perfectly and uniformly adhering to the glass. *Cadmium* and mercury unite with great ease, and the amalgam crystallizes in octoëdra, when composed of 100 mercury + 28 cadmium (an atom of each metal); it fuses at 167° . (STROMEYER.) The amalgams of *cobalt* and *nickel* have not been examined. Amalgam of *copper* may be made as follows:—To a hot solution of sulphate of copper, add a little hydrochloric acid and a few sticks of zinc, and boil the mixture for about a minute; by this means the copper will be precipitated in a metallic state, and in a finely-divided spongy form: take out the zinc, pour off the liquor, wash the copper with hot water, and pour upon it a little dilute nitrate of mercury, which will instantly cover every particle of copper with a coating of mercury: then add mercury to the amount of two or three times the weight of the copper, and a slight trituration will combine them so far that the completion of the process may be effected by heating the mixture for a few minutes in a crucible. (AIKIN'S *Dictionary*, Art. MERCURY.) *Lead* and mercury readily combine in all proportions: 3 parts of mercury and 2 of lead form a crystallizable amalgam. *Antimony* amalgamates difficultly, and forms a granular compound. *Bismuth* and mercury readily unite: 2 parts of mercury poured into 1 of melted bismuth form a compound which slowly solidifies and crystallizes. When mercury is combined with a little bismuth, lead may be added without greatly interfering with the fluidity of the compound. Dr. Thomson states that Beccher was the first who observed the remarkable fluidity of a mixture of 3 parts of mercury, 1 of lead, and 1 of bismuth, and that it may be squeezed through leather without decomposition: it is used for silvering the inside of glass balls which are previously made perfectly clean and warm. When mercury is adulterated, it is with these metals; but the facility with which it then oxidizes, and the imperfect fluidity of its small globules, render the fraud easy of detection. The action of

mercury on the other metals which have been described has not been examined, with the exception of that on *tellurium* and *arsenic*. With *tellurium*, it forms a granular compound: with *arsenic*, a gray amalgam of 5 parts of mercury and 1 of *arsenic*: the metals require to be stirred together for some hours over the fire. Dumas suggests the examination of the action of *arsenuretted* hydrogen on the chlorides of mercury.

AMALGAM OF AMMONIUM. METALLIZATION OF AMMONIA.—It was first observed by Berzelius and Pontin that when mercury is negatively electrized in a solution of ammonia, or of an ammoniacal salt, or when an amalgam of potassium and mercury is placed upon moistened sal-ammoniac, the metal increases in volume, and becomes of the consistency of butter, an appearance which has sometimes been called the *metallization of ammonia*. If mercury which has been amalgamated with about a fiftieth part of potassium be made the negative electrode in a solution of sal-ammoniac, the effect is produced to its greatest extent; the mercury puffs up to 80 or 100 times its original volume, and if, in this state, it be cooled to 32° , it crystallizes in cubes; the amalgam is lighter than water, but when left to itself, it gradually shrinks back again into mercury, evolving ammonia and hydrogen, not exceeding in weight a seventy-thousandth of that of the amalgam, and yet conferring upon it the semifluid or solid state, and susceptibility of crystallization; according to Gay Lussac and Thenard, the volume of the hydrogen is 347, and of the ammonia 422, to 100 volumes of mercury. These extraordinary phenomena have suggested several hypotheses concerning the nature of ammonia and its components, and also of the metals, respecting which the reader may consult Gay Lussac and Thenard (*Recherches Physico-Chimiques*, vol. i.), who, finding the amalgam resolvable into mercury, ammonia, and hydrogen, regard it merely as a compound of those substances; and Berzelius (*Lehrbuch*, i.), who considers the appearances as resulting from the combination of a metal, which he terms *ammonium*, with the mercury; this view of the subject gave rise to what has been called the *ammonium theory*, as has previously been explained (p. 436).

CHARACTERS OF THE SALTS OF MERCURY.—The soluble salts of the *protoxide* are mostly white, and of a metallic and nauseous taste. Some of them, when neutral, are resolved by water into basic and acid salts. Phosphorous and sulphurous acids, and protochloride of tin, precipitate metallic mercury: the caustic alkalis throw down a black powder; the carbonated alkalis, yellow or brown; the phosphates, white, even in very dilute solutions; sulphuretted hydrogen and the hydrosulphurets, black; hydriodic acid and the iodides, dingy green or yellow; hydrochloric acid and the chlorides, white and curdy; the alkaline chromates, red; ferrocyanuret of potassium, white; the oxalates, white, even when very dilute; tincture of galls, brownish-yellow. The soluble salts of the *peroxide* of mercury are mostly white when neutral, yellow when basic; they are poisonous, and nauseously metallic to the taste, and are often resolved by water into acid and basic salts. Ammonia and carbonate of ammonia produce white precipitates; iodide of potassium, a red; and infusion of galls, an orange precipitate. Unless in concentrated solution they are not

affected by hydrochloric or oxalic acids. Metallic mercury is precipitated from all its solutions by a plate of clean copper. The presence of organic substances interferes considerably with the appearances produced by some of the above tests; hence, in cases of poisoning by corrosive sublimate, peculiar precautions are sometimes required, and in all cases the precipitate should be collected and heated in a tube with a little white flux, or some such reducing agent, so as to separate metallic mercury, the microscopic globules of which are easily sublimed and discerned. (See CHRISTISON *on Poisons*, and ROSE'S *Analytical Chemistry*.) The insoluble mercurial salts are mostly volatilized at a red heat, and they are all decomposed, with the production of metallic mercury, when mixed with a little carbonaceous matter, and heated in a glass tube.

§ XXXI. SILVER.

THIS metal, the *Luna* or *Diana* of the alchemists (☽), was known at a very remote period; it is mentioned in the book of Job: it is found *native*, and in a variety of combinations; the most common of which is the *sulphuret*.

Native Silver has the general characters of the pure metal. It occurs in masses; arborescent; capillary; and, sometimes, crystallized in cubes and octoëdra. It is seldom pure, but contains small portions of other metals, which affect its colour and ductility. It is chiefly found in primitive countries. In Peru and Mexico are the richest known mines of native silver. The mines of Saxony, Bohemia, and Swabia, and those of Kongsberg in Norway, are the richest in Europe. It has been found in Cornwall and Devonshire.

Pure Silver may be procured by dissolving the standard silver of commerce in pure nitric acid, diluted with an equal measure of water. Immerse a plate of clean copper into the solution, which soon occasions a precipitate of metallic silver; collect it upon a filter; wash it with solution of ammonia, and then with water, and fuse it into a button.

It may also be procured by adding to the above solution of standard silver, a solution of common salt; collect, wash, and dry the precipitate, and gradually add it to twice its weight of fused carbonate of potassa in a red-hot crucible. Metallic silver is separated, and may be fused into a button.

Silver is of a more pure white than any other metal; it has considerable brilliancy, and takes a high polish. Its specific gravity varies between 10·4, which is the density of cast silver, and 10·5 to 10·6, which is the density of rolled or stamped silver. The specific heat of pure silver is 0·05701. (REGNAULT.) It is so malleable and ductile, that it may be extended into leaves not exceeding a ten-thousandth of an inch in thickness, and drawn into wire infinitely finer than a human hair. Silver melts at a bright red-heat, estimated by Mr. Daniell at 1873° of Fahrenheit's scale, and when in fusion appears extremely brilliant. It resists the action of air at high temperatures for a long time, and does not oxidize; the *tarnish* of silver is occasioned by sulphuretted hydrogen; it takes place very slowly upon the pure metal, but more rapidly upon the alloy with copper used

for plate, and was found by Proust to be sulphuret of silver. Pure water has no effect upon the metal; but if the water contain vegetable or animal matter, it often slightly blackens its surface, generally in consequence of the presence of sulphur. If an electric discharge be passed through fine silver-wire, it burns into black powder, which is probably an oxide of silver. In the Voltaic circle it burns with a fine green light, and throws off abundant fumes. Exposed to an intense white-heat in the open fire, it boils and evaporates, but in close vessels it is not sensibly volatile. If suddenly cooled, it crystallizes during congelation, often shooting out like a cauliflower, and *spirling* or throwing small particles of the metal out of the crucible. This arises, according to Lucas, from the sudden escape of oxygen, which the metal absorbs and retains whilst fluid, but suddenly gives it off when it solidifies: this property of absorbing oxygen is prevented by the presence of a quantity of copper, not exceeding 5 per cent. When nitre is thrown upon melted silver in a crucible, and the whole retained for about half an hour in fusion, it absorbs 20 times its volume of oxygen, which is given out on plunging the fused metal under a bell jar filled with water.

The analyses of the compounds of silver furnish data from which its equivalent may be estimated at 108, (108 GMELIN, PHILLIPS, and TURNER, 108.3 GRAHAM, 110 THOMSON, 107.97 PENNY.)

REDUCTION OF SILVER ORES.—Silver is not unfrequently obtained in considerable quantities from *argentiferous sulphuret of lead*, which is reduced in the usual way, and the argentiferous lead is then fused in a shallow dish, placed in a reverberatory furnace, with a current of air constantly passing over its surface; in this way the lead is converted into *litharge*, and the silver, not being thus oxidized, is left in the metallic state; it is fused in a porous crucible, called a *cupel* or *test*, by which the remaining lead is entirely separated, and a button of pure silver remains. The litharge which results from this operation is afterwards itself reduced by charcoal, and furnishes lead which is almost free from silver, the ordinary lead of commerce generally containing a trace of the latter metal, and being consequently unfit for certain purposes of the arts, especially for the manufacture of white-lead (p. 846). Some of the silver ores, especially the *sulphurets*, are reduced by *amalgamation*. The ore, when washed and ground, is mixed with a portion of common salt and roasted: during this operation sulphate of soda and chloride of silver are formed: the product is then powdered, and agitated with mercury, water, and filings or fragments of iron; in this operation the chloride of silver is decomposed, chloride of iron is formed which is washed away, and the silver and mercury combine into an amalgam, from which the excess of mercury is first squeezed out in leather bags, and the remainder driven off by distillation. The old process of *eliquation* is now scarcely used: it consisted in fusing alloys of copper and silver with lead; this triple alloy was cast into round masses, which were set in a proper furnace upon an inclined plane of iron with a small channel grooved out, and heated red-hot, during which the lead melted out, and in consequence of its attraction for silver, carried that metal with it, the copper being left behind in a reddish-black spongy mass. (AIKIN'S Dictionary, ART. SILVER.)

OXIDES OF SILVER.—There are three oxides of this metal, a suboxide, a protoxide, and a binoxide; of these, the protoxide only forms permanent and definite saline combinations.

SUBOXIDE OF SILVER. ($2ag + o$).—This oxide was first obtained by Faraday, by exposing an ammoniacal solution of the protoxide to the action of air; it separates in the form of a black film. (*Quarterly Journal*, v. 368.) Wöhler obtained it by the action of hydrogen on citrate of silver at the temperature of 212° ; the protoxide contained in that salt loses under such circumstances half of its oxygen, and the suboxide remains combined with half of the acid. "The solution in water of the suboxide salt is dark-brown, and the suboxide is precipitated black from it by potash; when the solution of the subsalt is heated it becomes colourless, and metallic silver appears in it; the salt dissolves of a brown colour in ammonia. Several other salts of silver, containing organic acids, comport themselves in the same way as the citrate when heated in hydrogen." (GRAHAM.)

PROTOXIDE OF SILVER ($ag + o$) or Ag , may be obtained by adding lime or baryta-water, or dilute solution of potassa, to the solution of nitrate of silver, and washing the precipitate. It is of a dark olive colour, anhydrous, tasteless, but soluble, according to Graham, to a small extent in pure water free from saline matter, and, like oxide of lead, has when in solution an alkaline reaction. When gently heated, it is reduced to the metallic state; long exposure to light also reduces it, converting it into a black powder, which is either silver or its suboxide. It confers a yellow colour upon glass, and is employed in enamel and porcelain painting. Its specific gravity is 7.14 (HERAPATH). It consists of

				Berzelius.	Davy.	Gay Lussac and Thenard.
Silver	1	108	93.103	93.112	93.1	92.937
Oxygen	1	8	6.897	6.888	6.9	7.063
Protoxide of silver	1	116	100.000	100.000	100.0	100.000

PEROXIDE OF SILVER. ($ag + 2o$).—Ritter, by electrizing a weak solution of silver, observed the deposition of acicular crystals at the positive pole, which, according to Grothuss, dissolve in nitric acid, without decomposition, and are a *peroxide of silver*. Ammonia energetically decomposes this compound, and sulphuric and phosphoric acids convert it into the protoxide. (GEHLEN'S *Journ.*, iii.)

AMMONIURET OF SILVER. ARGENTATE OF AMMONIA.—Oxide of silver readily dissolves in ammonia, and, by particular management, a *fulminating silver*, composed probably of the oxide combined with ammonia, may be obtained. It was discovered by Berthollet. (*Ann. de Ch.*, i.) The best process for preparing it is to pour a small quantity of liquid ammonia upon the oxide; a portion is dissolved, and a black powder remains, which is the detonating compound; it is also precipitated by potassa from the ammonio-nitrate of silver. It explodes when gently heated; nitrogen and water are instantaneously evolved, and the silver is reduced. The oxide of silver should be perfectly pure and thoroughlyedulcorated, and the ammonia quite free from carbonic acid. It should only be prepared

in small quantities, and handled with the greatest caution, many accidents having arisen from its careless management. It sometimes explodes while still wet. It is soluble in ammonia: it is immediately decomposed by hydrochloric acid, which forms chloride of silver and sal-ammoniac; and by sulphuretted hydrogen, which forms sulphuret of silver, and hydro-sulphuret of ammonia; with sulphuric acid, it affords sulphate of silver, and of ammonia, but nitrogen is also evolved. The real nature of this compound is probably not at present understood.

CHLORIDE OF SILVER. (*ag + c.*)—This compound is easily procured by adding a solution of chlorine, of hydrochloric acid, or of common salt, to a solution of nitrate of silver, or, indeed, to any of the soluble salts of silver, with the exception of the hyposulphite. It falls in the form of a curdy precipitate, of a white colour, but which, by exposure to light, becomes brown, and ultimately black. This happens even in diffused daylight, but in sunshine the change is extremely rapid, more especially if any trace of organic matter be present. This property of the chloride has led to its application for purposes of photogenic drawing. (See *Nitrate of Silver*.) When a small quantity of chloride of mercury is precipitated along with the chloride of silver, the blackening effect of light is greatly diminished. It is perfectly insoluble in water; so that the minutest portion of hydrochloric acid, or of a chloride in solution, may be detected by adding to the liquid a drop or two of nitrate of silver; it becomes opalescent and gray or brown by exposure to light. It is sparingly dissolved by concentrated hydrochloric acid, and thrown down upon dilution: when the hydrochloric solution is carefully evaporated, the chloride is deposited in the form of octoëdral crystals. It is insoluble in nitric acid, and in cold sulphuric acid, but when boiled in sulphuric acid, it is very slowly decomposed. When dry chloride of silver is heated to dull redness in a silver crucible, it does not lose weight, but fuses, and, on cooling, concretes into a gray semitransparent substance, (sp. gr. 5.45,) which has been called *horn silver*, or *luna cornea*. If slowly cooled, Proust has remarked that it has a tendency to octoëdral crystallization. Heated to a bright red or white heat in an open vessel, it volatilizes in dense white fumes. Scheele was the first who examined the cause of the blackening effect of light upon this chloride, and the curious results of his researches have already been referred to (p. 200). He found that the metal was partially reduced, and hydrochloric acid formed; hence moisture is necessarily present. Seebeck found that white chloride of silver might be exposed, without change of colour, when covered in a stopped phial, with sulphuric acid; but if the phial was open, the blackening ensued; as it did also when water was added. Hydrogen gas, and substances affording hydrogen, decompose moist chloride of silver: they reduce it to the metallic state, and the chlorine is carried off in the form of hydrochloric acid; in the dark, perfectly pure hydrogen does not discolour the chloride.

If fused with twice its weight of potassa or soda, chloride of silver is decomposed, and a globule of metallic silver is obtained. This reduction is best effected by projecting the dry chloride upon twice its weight of fused carbonate of potassa, or upon the fused mixture of the carbonates of potassa and soda. It is also rapidly decomposed, when moist, by tin

and zinc, and by many of the other metals, especially if a little hydrochloric acid be added. Triturated with zinc-filings and moistened, the heat produced is so considerable as to fuse the resulting alloy of zinc and silver. (FARADAY, *Quarterly Journal of Science and Arts*, viii. 374.) When a lump of chloride of silver is put with zinc or iron filings into diluted sulphuric acid, the reduced silver retains the original form of the chloride, the evolved hydrogen therefore appears to be the reducing agent. Chloride of silver is not reduced when heated with pure carbon, but the ordinary charcoals decompose it in consequence of their containing hydrogen.

Chloride of silver is very soluble in ammonia, a circumstance by which it is usefully distinguished from some other chlorides, which, like it, are white, and formed by precipitation; but we should be cautious in applying heat to the ammoniacal solution, as it sometimes forms a precipitate of fulminating silver: it also furnishes crystals which are often explosive, and which, when exposed to air, or put into water, lose their transparency, evolve ammonia, and crumble into chloride of silver. The fused chloride, exposed to ammoniacal gas, absorbs a considerable portion, which is given off by heat. If the dry chloride, thus saturated with ammonia, be thrown into chlorine, the ammonia spontaneously inflames. (FARADAY, *Journal of Science and Arts*, v. 75.) Chloride of silver is soluble in and decomposed by all the liquid hyposulphites: it is also soluble in a solution of sal-ammoniac, and of the chlorides of potassium and sodium, and these solutions may be used in the process of silvering copper or other metals: they afford double chlorides on evaporation, which may be obtained crystallized, but which have not been examined in detail: they are decomposed by water.

As chloride of silver is insoluble in water, and very readily formed, it is often employed in quantitative analysis, as a means of ascertaining the proportion of chlorine present in various compounds. In these cases some excess of the precipitant should be used, and the precipitate allowed to subside previous to separating it upon the filter: if the supernatant liquor become perfectly clear, the whole of the silver has fallen; if it remain opalescent, a portion is probably still retained. When the precipitate remains long suspended, its deposition may be accelerated by heat, or by adding a little nitric acid. The chloride in these cases should be perfectly dried in a silver crucible, up to incipient fusion.

Chloride of silver consists of

					Wenzel and		Marcet and		
					Berzelius.	Gay Lussac.	J. Davy.	Turner.	
					Rose.				
					Bucholz.				
Silver	. . . 1	. 108	. 75	. 75	. 75.18	. 75.33	. 75.25	. 75.5	. 75.3
Chlorine	. . . 1	. 36	. 25	. 25	. 24.82	. 24.67	. 24.75	. 24.5	. 24.7
Chloride of silver }	1	144	100	100	100.00	100.00	100.00	100.0	100.0

Native Chloride of Silver has been found in most of the silver-mines; it occurs massive, and crystallized in small cubes and octoëdra.

CHLORATE OF SILVER ($\text{Ag} + \text{Cl}$) is formed by digesting oxide of silver in chloric acid: it forms small rhombic crystals, which, by the action of chlorine, are converted into chloride of silver. They are soluble in 4 parts of water at 60° . (CHENEVIX. VAUQUELIN.)

IODIDE OF SILVER ($ag + i$) is precipitated upon adding hydriodic acid, or a soluble iodide, to a solution of nitrate of silver. It is of a dingy-yellow colour, insoluble in water, and decomposed when heated with potassa. It is particularly characterized by being insoluble in ammonia. When fused it acquires a red colour. It volatilizes before the blowpipe, leaving a little silver only behind. It is discoloured by light. (In reference to the use of iodine and iodic compounds in photogenic drawing, see SIR J. HERSCHEL, *Phil. Trans.*, 1840: also MR. R. HUNT's and MR. ALFRED TAYLOR's *Pamphlets*.) Concentrated nitric and sulphuric acid decompose it. It dissolves in concentrated solutions of the alkaline chlorides, and combines also with iodide of potassium and the other alkaline and earthy iodides. A thin film of iodine upon a plate of silver is used in Daguerre's photographic process, the plate of silvered copper intended to receive the image in the camera being prepared by exposing it in a box containing iodine: the light seems to act upon this film rather than upon an iodide of silver. It consists of

Silver . . .	1	108	46.4
Iodine . . .	1	126	53.6
Iodide of silver	1	234	100.0

Native Iodide of Silver has been found in some of the Mexican ores, associated with native silver, sulphuret of lead, and carbonate of lime: it was analyzed by treating it first with acetic acid which abstracted the carbonate of lime; then by nitric acid, to remove the native silver and leave a mixture of sulphate of lead with the iodide of silver: the latter is decomposed by heating it in a current of dry chlorine; chloride of iodine passes off and chloride of silver remains. (VAUQUELIN. DUMAS.)

IODATE OF SILVER ($Ag + i'$) is precipitated in the form of a white powder by adding iodic acid or iodate of potassa to a solution of nitrate of silver. It is very soluble in ammonia. It is decomposed by sulphurous acid, which throws down iodide of silver, and becomes sulphuric acid. (GAY LUSSAC.)

BROMIDE OF SILVER ($ag + b$) is an insoluble yellowish substance thrown down upon the addition of bromine, or hydrobromic acid, or the soluble bromides, to nitrate of silver: it is fusible, and like the chloride it dissolves in ammonia (BALARD, *Ann. de Ch. et Ph.*, xxxii. 361): it consists of

Silver . . .	1	108	58
Bromine . . .	1	78	42
Bromide of silver	1	186	100

BROMATE OF SILVER, not described.

FLUORIDE OF SILVER ($ag + f$) is a soluble compound, which does not crystallize. When heated it fuses; and at a higher temperature, and exposed to air, it is slowly reduced. (BERZELIUS, *Ann. de Ch. et Ph.*, xi. 121.)

NITRITE OF SILVER.—This salt is obtained by boiling powdered silver in nitric acid already saturated with silver: or nitrate of soda may be fused till converted into nitrite, when it precipitates silver brown; if this salt be then dissolved in boiling water, precipitated by nitrate of silver,

and the solution filtered while hot, nitrite of silver separates as the solution cools; it requires 120 parts of water at 60° for its solution. (See PROUST's Paper in NICHOLSON's *Journal*, xv. 376.)

NITRATE OF SILVER. ($\text{Ag} + n/$).—Nitric acid, diluted with 3 parts of water, readily dissolves silver, with the disengagement of nitric oxide gas. If the acid contain the least portion of hydrochloric acid, the solution will be turbid, and deposit a white precipitate; and if the silver contain copper, it will have a permanent bluish hue; or if gold, that metal will remain undissolved in the form of a black powder.

The solution of nitrate of silver should be perfectly clear and colourless; it is caustic, and tinges animal substances of a deep yellow, which, by exposure to light, becomes a deep purple, or black stain, and is indelible, or peels off with the cuticle: it consists of reduced silver. Nitrate of silver may be obtained in white anhydrous crystals, in the form of four and six-sided tables or thin plates: by slow evaporation it forms right rhombic prisms. (BROOKE, *Ann. of Phil.*, 2nd series, vii. 162.) They have a bitter and metallic taste, and are soluble in about their own weight of water at 60° , and half their weight at 212° . Alcohol also dissolves about one-fourth its weight of this salt, at its boiling-point, but deposits nearly the whole as it cools. The solution of this salt is quite neutral to the test of litmus. According to Proust (NICHOLSON's *Journal*, xv. 376), a solution of this nitrate, when boiled with finely-divided silver, dissolves a portion, and yields a solution containing a suboxide of silver, but no *sub-nitrate* of silver has been formed.

Nitrate of silver blackens when exposed to light, and when thus acted upon, is no longer perfectly soluble in water, owing to the separation of a portion of metallic silver. When heated in a silver crucible it fuses into a gray mass, and if cast into small cylinders, forms the *lapis infernalis*, or *lunar caustic* of pharmacy; the *argenti nitras* of the *Pharmacopœia*. In forming this preparation, care should be taken not to overheat the salt, so as to blacken it, and the moulds should be warmed. Exposed to a red heat, the acid is partly evolved and partly decomposed, and metallic silver obtained. Sulphur, phosphorus, charcoal, hydrogen, and several of the metals, decompose this nitrate. A few grains mixed with a little sulphur, and struck upon an anvil with a heavy hammer, produce a detonation; phosphorus occasions a violent explosion when about half a grain of it is placed upon a crystal of the nitrate, upon an anvil, and struck sharply with a hammer; and if heated with charcoal it deflagrates, and the metal is reduced.

If a piece of silk dipped into a solution of nitrate of silver be exposed, while moist, to a current of hydrogen gas, it is first blackened, and afterwards becomes iridescent from the reduction of portions of the metal. (MRS. FULHAME's *Essay on Combustion*.) Ivory, marble, and several other bodies, may be stained black, or even silvered, by soaking them in a solution of nitrate of silver, and fully exposing them to the action of the sun's rays. When the vapour of pure distilled water is made to pass through nitrate of silver, the solution assumes all the shades between yellow and dark-brown, according to its concentration and the time the steam has passed through it. When it has acquired the temperature of 212° , its colour

increases rapidly. Nitric acid immediately destroys this colour, the cause of which is referred by Pfaff to the deoxidizing agency of the steam. (*Quarterly Journal*, xvi. 162.) A stick of phosphorus, introduced into a solution of nitrate of silver, soon becomes beautifully incrustated with the metal, which separates upon it in arborescent crystals. A plate of copper occasions a brilliant precipitation of crystalline silver, and the copper is oxidized and dissolved by the acid. Mercury introduced into the solution of nitrate of silver, causes a beautiful crystalline deposit of silver, called the *arbor Dianæ*: it was first remarked by Lemery. To obtain this crystallization in its most perfect state, the solution should contain a little mercury, and the mercury put into it should be alloyed with a little silver. Baumé directs an amalgam of 1 part of silver with 7 of mercury, of which a small piece is to be introduced into a solution composed of 6 drachms of saturated nitrate of silver and 4 drachms of a similar solution of mercury diluted with 5 ounces of distilled water: a small flask or matrass should be used for the experiment, kept perfectly at rest: in a few minutes small filaments of silver darken the surface of the amalgam, and in about eight and forty hours the whole has separated in a shrub-like form. The addition of mercury to the solution, and of silver to the precipitating mercury, is said to give a degree of tenacity to the arborescent deposit of crystals, which prevents their falling to the bottom of the flask.

The alkaline metallic oxides decompose nitrate of silver; it is also decomposed by hydrochloric, sulphuric, phosphoric, and boracic acids. The protosulphate of iron throws down metallic silver when added to a solution of the nitrate; protochloride of tin forms a gray precipitate, consisting of peroxide of tin and oxide of silver. Ammonia, added to solution of nitrate of silver, occasions a precipitate, soluble in excess of the alkali. (See BERTHOLLET'S *Fulminating Silver*, p. 802.)

Nitrate of silver is employed for writing upon linen, under the name of *indelible* or *marking ink*, which may be prepared by dissolving 2 drachms of pure nitrate of silver and 1 drachm of gum arabic in 7 drachms of distilled water, coloured by a little China ink. The preparatory liquid for moistening the cloth is made by dissolving 2 ounces of crystallized carbonate of soda and 2 drachms of gum arabic in 4 ounces of water. "For this ink, which is expensive, another liquid has been substituted by bleachers, namely, coal tar made sufficiently thin with naphtha to write with, which is found to resist chlorine, and to answer well as a marking ink." (GRAHAM.) Nitrate of silver is an ingredient in some of the liquids which are sold for the purpose of changing the colour of hair. It is used in medicine; and in surgery, as an excellent caustic. When taken internally, a very disagreeable effect frequently follows its use, which is the discoloration of the *rete mucosum*; so that the whole surface of the body, and especially the parts most exposed to light, acquire a leaden-gray or livid colour, which is permanent, and can neither be removed nor prevented.

Solution of nitrate of silver is a valuable test of the presence of chlorine, hydrochloric acid, and the soluble chlorides, with which it forms a white cloud when very dilute, but a flaky precipitate when more concentrated; the precipitate is soluble in ammonia, but insoluble in nitric acid. Heat, agitation, or the addition of a few drops of nitric acid, so as to render the

liquid sour, facilitate the deposition of the precipitate. The hydriodic, hydrobromic, and hydrocyanic acids, also occasion white precipitates in solution of nitrate of silver, which blacken by exposure to light. Its application as a test for arsenic and arsenious acids has already been noticed. Gallic and tannic acid, and the varieties of extractive matter, discolour nitrate of silver without the aid of light. A peculiar extractive matter sometimes occurs in rough nitre, which also causes its solution to blacken nitrate of silver. Some spring and mineral waters contain a substance producing a similar effect.

Nitrate of silver is an anhydrous salt, composed of

					Proust.
Oxide of silver	1	.	.	116	68.24
Nitric acid	1	.	.	54	31.76
<hr/>					<hr/>
Nitrate of silver	1			170	100.00
					100.0

AMMONIO-NITRATE OF SILVER.—Ammonia is rapidly absorbed by nitrate of silver, with the production of heat sufficient to fuse the compound, which is white, coherent, and consists of 100 parts of the nitrate + 29.5 ammonia. Mitscherlich has described an analogous compound formed in the humid way. (*Ann. de Ch. et Ph.*, Lxii. 314; *Poggend. Ann.*, ix. 413.) An ammonio-nitrate of silver is also obtained when ammonia is added to a solution of nitrate of silver till the first-formed precipitate is entirely redissolved. This solution forms a good marking ink, and has also been used in the preparation of paper for photogenic drawing.

SULPHURET OF SILVER. (*ag + s.*)—Silver readily combines with sulphur, and produces a gray crystallizable compound, considerably more fusible and much softer than silver. It may be obtained by heating finely-divided silver or plates of silver with sulphur. Its density is 7.2.

Sulphuretted hydrogen and hydrosulphuret of ammonia occasion a copious black precipitate of sulphuret of silver when added to solutions of the metal: sometimes a portion of the silver is apparently at the same time reduced to the metallic state. It is the presence of some form of sulphur, generally sulphuretted hydrogen, which occasions the tarnish upon silver, and which, though only superficial, is a great obstacle to many applications that might otherwise be made of this beautiful metal. Sulphuret of silver consists of

					Vauquelin.	Berzelius.	Wenzel.
Silver	1	.	.	108	87.1	87.27	85.5
Sulphur	1	.	.	16	12.9	12.73	14.5
<hr/>					<hr/>		
Sulphuret of silver	1			124	100.0	100.00	100.0

Native Sulphuret of Silver, or *vitreous silver-ore*, is found in various forms, and when crystallized is in cubes, octoëdra, and dodecaëdra. It is soft and sectile. The finest specimens are from Siberia. The method of its reduction has been above described. A triple combination of *silver*, *antimony*, and *sulphur*, constitutes the *red* or *ruby silver-ore*; it is found massive and crystallized in hexaëdral prisms. It consists of about 70 parts of sulphuret of silver, and 30 of sulphuret of antimony; or, according to Bonsdorff, of 3 atoms of silver, 2 of antimony, and 6 of

sulphur. It occurs in all the silver-mines, and is sometimes accompanied by the *brittle sulphuret of silver*, or *silver glance*, and by *antimonial silver* ($2\text{ ag} + \text{an}$).

HYPOSULPHITE OF SILVER ($\text{Ag} + \bar{\text{s}}$) has been examined by Herschel. (*Edin. Phil. Journal*, i. 26.) It is formed by dropping a weak solution of nitrate of silver into a very dilute solution of hyposulphite of soda: a white cloud is at first produced, which redissolves on agitation; on adding more of the precipitant, the cloud reappears and aggregates into a gray precipitate, which appears to consist of hyposulphite of silver; the supernatant liquor tastes intensely sweet, which is remarkable, considering the disgusting bitterness both of the nitrate and of the hyposulphite, and shows, "how little we know of the way in which bodies affect the organs of taste. Sweetness and bitterness, like acidity, seem to depend upon no particular principle, but to be regulated by the state of combination in which the same principles exist at different times." Hyposulphite of silver is also produced when chloride of silver is dissolved in any of the hyposulphites; the solution is intensely sweet without any metallic flavour. These facts show the strong affinity that exists between oxide of silver and hyposulphurous acid. The solubility of argentine compounds in hyposulphites has led to an important application of them in photogenic drawing, for the purpose of fixing the designs, by the removal of all adhering or unchanged salt of silver. (See HERSCHEL, A. TAYLOR, &c.) Hyposulphite of silver is very prone to decomposition, so as to form sulphate of oxide of silver, and sulphuret of silver; hence the occasional blackening of its solutions.

HYPOSULPHITE OF POTASSA AND SILVER is formed when liquid potassa is dropped into the solution of chloride of silver in hyposulphite of soda; it separates in the form of a copious precipitate, which, when washed and dried, is found to consist of small gray pearly scales; they are difficultly soluble in water; of a very sweet taste; and, heated before the blowpipe, afford a bead of silver. Several other analogous double salts have been described by Herschel.

SULPHITE OF SILVER ($\text{Ag} + \bar{\text{s}}$) is obtained in crystalline grains by digesting oxide of silver in sulphurous acid, or by adding an alkaline sulphite to a solution of silver. It produces double salts with the sulphites of the alkalis. According to Fourcroy, it is not blackened by exposure to light, nor altered by air.

HYPOSULPHATE OF SILVER ($\text{Ag} + \text{s}'$) is formed by digesting carbonate of silver in hyposulphuric acid: it crystallizes in permanent prismatic crystals, soluble in 2 parts of cold water, and contains 2 proportionals of water of crystallization. Excess of ammonia added to a solution of this salt occasions a gradual precipitation of crystalline grains, consisting of an *ammonio-hyposulphate of silver*. (HEEREN.)

SULPHATE OF SILVER ($\text{Ag} + \text{s}'$) is deposited when sulphate of soda is mixed with nitrate of silver. It is also formed by boiling silver with its weight of sulphuric acid. It forms a white saline mass, easily fusible.

It requires about 90 parts of water at 60° for its solution; in boiling water it is more soluble, and is deposited, as the solution cools, in small anhydrous prismatic crystals: it is decomposed at a red heat, and leaves metallic silver: it dissolves in sulphuric acid, and on moderate dilution the greater part of the salt again falls down; the best crystals of sulphate of silver are obtained from its solution in diluted sulphuric acid.

Upon the large scale, small portions of gold may be most economically separated from large quantities of silver, by heating the finely granulated alloy in sulphuric acid: the gold remains in the form of a black powder, and the sulphate of silver may be decomposed by the action of metallic copper; the silver is precipitated in a pulverulent state, and, with a little borax or other vitrifiable flux, is fused, and cast into ingots: the sulphate of copper is easily obtained in the crystallized state by evaporating the residuary liquid.

A compound acid, which may be called *nitrosulphuric*, consisting of 1 part of nitre dissolved in about 10 of sulphuric acid, dissolves silver at a temperature below 200° , and the solution admits of moderate dilution before sulphate of silver separates from it. This acid scarcely acts upon copper, lead, or iron, unless diluted with water; it is, therefore, useful in separating the silver from old plated articles; the precious metal may afterwards be separated either in the form of chloride, by adding common salt; or by diluting the acid and continuing the immersion of the pieces of copper which have lost their silvering, and which will now dissolve in the diluted acid, and occasion the precipitation of metallic silver. (KEIR, *Phil. Trans.*, LXXX.)

Sulphate of silver consists of

Oxide of silver	. . 1 . .	116 . .	74.4
Sulphuric acid	. . 1 . .	40 . .	25.6
Sulphate of silver	1	156 . .	100.0

AMMONIO-SULPHATE OF SILVER.—100 parts of sulphate of silver slowly absorb 11.82 of dry ammonia. In the humid way, Mitscherlich formed a double salt containing twice as much ammonia. (H. ROSE, *Ann. de Ch. et Ph.*, lxii. 314.)

PHOSPHURET OF SILVER (*ag + p*) is a white brittle compound; it is formed either by projecting phosphorus upon red-hot silver, or by heating a mixture of 1 part of silver-filings, 2 of vitrified phosphoric acid, and 0.5 of charcoal. It loses its phosphorus when fused and exposed to air. Pelletier observed, in regard to this phosphuret, that the fused silver was capable of retaining a larger proportion of phosphorus in combination than after it had solidified; for the fused phosphuret, when it concretes, throws off a quantity of phosphorus, producing a brilliant combustion: there is an analogy between this effect and the similar absorption and evolution of oxygen. The concreted phosphuret consists of 108 silver + 16 phosphorus.

HYPOPHOSPHITE and PHOSPHITE OF SILVER have not been examined; probably oxide of silver would be reduced by these acids.

PHOSPHATE OF SILVER.—When the neutral phosphate of soda is added to nitrate of silver, a yellow anhydrous precipitate falls, which is

fusible at a white heat, and soluble in nitric acid, and in phosphoric acid, and quickly discoloured by exposure to light: its specific gravity is 7.3: when heated it becomes brown, but regains its yellow tint as it cools. It consists of

					Berzelius.
Oxide of silver	1½	174	82.86	82.975	
Phosphoric acid	1	36	17.14	17.025	
Phosphate of silver	1	210	100.00	100.000	

When this salt is dissolved in phosphoric acid, a part of it is deposited in granular crystals, and by spontaneous evaporation of the residuary solution, white plumose crystals, probably of the neutral phosphate of silver, are deposited.

PYROPHOSPHATE OF SILVER is the *white* precipitate thrown down from nitrate of silver by pyrophosphate of soda: Stromeyer found in it 75.39 oxide of silver + 24.61 pyrophosphoric acid; when it is boiled with phosphate of soda, yellow phosphate of silver and pyrophosphate of soda are formed.

SELENIURET OF SILVER (*ag + se*), obtained by precipitating nitrate of silver by seleniuretted hydrogen, is a black powder, which fuses into a globule having a metallic lustre. It consists of 73.16 silver + 26.84 selenium. When silver is fused with selenium, a gray *biseleniuret* is formed, from which excess of selenium is expelled by heat. (BERZELIUS.)

SELENITE OF SILVER is thrown down in the form of a white powder, very sparingly soluble in hot water. It is fusible, and at a high heat gives out selenious acid and oxygen, and leaves metallic silver. It is not discoloured by exposure to daylight. It may be obtained by boiling seleniuret of silver in nitric acid: as the solution cools the selenite is deposited in small crystals; or it may be thrown down, by dilution, in the form of a white powder.

CARBONATE OF SILVER is precipitated in the form of a white insoluble powder, by adding carbonate of potassa to nitrate of silver. It blackens by exposure to light, and is easily decomposed by heat. Carbonate of ammonia only throws down a portion of the silver from the nitrate, and forms a triple *ammonio-carbonate of silver*.

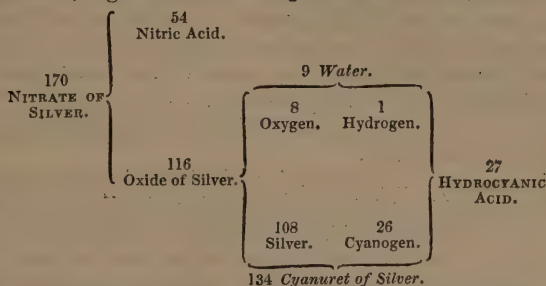
BORATE OF SILVER is thrown down from the nitrate of silver in the form of a white crystalline powder, by adding solution of boracic acid. It is very difficultly soluble in water. When a dilute solution of borax is added to nitrate of silver, oxide, and not borate of silver, is thrown down: a bibasic borate falls when the solutions are strong. (H. ROSE.)

CYANURET OF SILVER. (*ag + cy*).—Hydrocyanic acid causes a white precipitate in solution of nitrate of silver, which is *cyanuret of silver*, and which, when heated, fuses, and, at a high temperature, gives out cyanogen. It is insoluble in water and in fixed alkalis, but readily soluble in ammonia. It is easily decomposed by hydrochloric acid, and by sulphuretted hydrogen; but sulphuric and nitric acids scarcely act upon it, unless concentrated and heated. It dissolves in a strong solution of nitrate of silver, and forms a compound which may be crystallized, but which is

decomposed by solution in water. This cyanuret has a place in the Pharmacopœia as an occasional source of hydrocyanic acid: it consists of

Silver	1	108	80.6
Cyanogen . . .	1	26	19.4
<hr/>			
Cyanuret of silver	1	134	100.0

The following diagram shows the theory of its decomposition by hydrochloric acid, together with the equivalents of the products:—



ARGENTO-CYANURETS.—Cyanurets of the alkaline bases form soluble double salts with cyanuret of silver; they are insoluble in alcohol, which throws them down from their aqueous solutions. The *argento-cyanuret of potassium* yields plumose colourless crystals: it produces precipitates in many of the metallic solutions, which are *insoluble argento-cyanurets*, corresponding in composition with the ferrocyanurets.

FERROCYANURET OF SILVER falls as a white powder when ferrocyanuret of potassium and nitrate of silver are mixed.

SULPHOCYANURET OF SILVER falls in the form of a white curdy precipitate when sulphocyanuret of potassium is added to nitrate of silver. It slowly blackens by exposure to light. It is insoluble in water, but soluble in ammonia, from which it crystallizes in brilliant white plates.

CYANATE OF SILVER.—When cyanate of potassa is added to nitrate of silver a white powder falls, somewhat soluble in hot water, and soluble in ammonia, with which it forms a white crystalline compound, but from which the ammonia may be expelled by heat; it blackens when heated, and burns with deflagration, the products being cyanic acid, carbonic acid, nitrogen, and dicyanuret of silver. (LIEBIG.)

FULMINATE OF SILVER. FULMINATING SILVER. $2(ag + o) + (2cy + 2o)$ or $(2Ag + ful')$.—This curious and dangerous compound is prepared as follows:—100 grains of fused and finely-powdered nitrate of silver are added to an ounce of warm alcohol, and the mixture stirred in a sufficiently large glass basin; an ounce of fuming nitric acid is then added, and presently a violent effervescence ensues and a powder falls: as soon as this appears white, cold water is added, and the powder is immediately to be collected upon a filter, washed, and carefully dried at a temperature of 100° . In collecting and handling this powder, the utmost caution is requisite; it should be made in small quantities only, and touched with nothing hard, for it has sometimes exploded upon the contact of a glass

rod, even under water: the feather of a common quill serves to collect it; and it should be kept in a wide-mouthed vessel covered by paper, and by no means in a stoppered or even a corked phial, as serious accidents have arisen from its unexpected explosion. In short, one cannot be too careful in meddling with it, and its use for fulminating balls and other purposes of amusement is highly dangerous.

Berzelius observes that, in preparing fulminating silver, a vessel of sufficient capacity should be used to prevent the liquid running over during the effervescence, by which portions of the powder are deposited upon its exterior, and apt to explode when dry; that all approach of flame should be avoided during the escape of the nitrous etherized gas, because its inflammation would probably occasion the powder to explode; and that care should be taken to avoid introducing all hard substances to stir or touch the precipitate.

Liebig's process for the preparation of fulminating silver differs a little from the above, and is as follows:—A drachm of refined silver is dissolved in half an ounce of nitric acid, specific gravity 1·36 to 1·38; two ounces of alcohol, specific gravity 0·85, are then added, and the whole heated in a matrass; white flocculi soon appear, and when ebullition begins the heat is to be withdrawn; the effervescence, however, continues, and the powder falls; when action ceases, the powder is to be collected with the precautions above described.

Fulminating silver is a gray crystalline powder; it acquires a dingy hue by exposure to light; it dissolves in about 40 parts of boiling water, and as the solution cools, it is deposited in minute crystals. It detonates in the quantity of a grain, or even half a grain, with great violence, when heated, or touched by any hard body; placed upon a piece of rock-crystal, and touched in the slightest manner by another crystal, it explodes violently; upon the contact of sulphuric acid, and by the electric spark, it also detonates. The nature of this substance has been investigated by Liebig and Gay Lussac (*Ann. de Ch. et Ph.*, xxiv. and xxv.), who have shown that it is a compound of 2 atoms of oxide of silver with 1 of fulminic acid (p. 564). Its components therefore are

					Gay Lussac and Liebig.				
Oxide of silver . . .	2	232	77·34	77·528	Fulminic acid	2	232	77·34	
Cyanogen . . .	2	52	17·33	17·160		1	68	22·66	
Oxygen . . .	2	16	5·33	5·312					
Fulminate of silver	1	300	100·00	100·000		1	300	100·00	

BIFULMINATE OF SILVER is produced by digesting the preceding in solution of potassa, filtering, and adding nitric acid; a precipitate falls, soluble in boiling water, from which crystals separate on cooling, composed of 1 atom of acid, and 1 of oxide of silver, and which are dangerously explosive. The formula, therefore, of this salt is $(ag + o) + (2cy + 2o)$.

FULMINATE OF POTASSA. ARGENTO-FULMINATE OF POTASSA.—When solution of potassa (or other alkaline base) is digested with fulminating silver, half the oxide of silver is thrown down, and, on filtering and carefully evaporating the solution, white foliated crystals may be obtained, of a metallic taste, neutral to tests, soluble in 8 parts of boiling water, and not precipitated by chlorides. They explode by heat and friction. In

this, and analogous compounds, therefore, the bifulminate of silver acts the part of an *acid* to the bases. This salt of potassa is composed of

Potassa	1	48	20·7	20·7
Oxide of silver	1	116	50·0 { Argento-cyanic	} 79·3
Fulminic acid	1	68	29·3 { acid,	
	1	232	100·00	100·0

Fulminating mercury is, as above stated (p. 949), a compound of protoxide of mercury and fulminic acid, and, when decomposed by the fixed alkalis, the mercury constitutes a part of the triple detonating salt, which may be called a *mercurio-fulminate*; and for mercury, some other metals may be substituted. When fulminate of silver or of mercury is digested with metallic copper, the solution furnishes green explosive crystals of *fulminate of copper*, $^2(Cu + O) + (2cy + 2O)$.

CYANURATE OF SILVER.—If nitrate of silver be added to cyanurate of potassa, a white precipitate is obtained, which consists of 1 atom of cyanuric acid, 2 of oxide of silver, and 1 of water ($3cy + 3O$) + ($ag + O$) + q . This salt heated in the dry state evolves hydrated cyanic acid. But if a solution of silver be added to a boiling solution of cyanurate of ammonia, containing ammonia in excess, the cyanurate, with 3 atoms of oxide of silver, is formed ($3cy + 3O$) + $3(ag + O)$. It is insoluble in water, very sparingly soluble in dilute nitric acid, may be heated to 600° without decomposition, is white, not blackened by light, and at a red heat emits carbonic acid and nitrogen, and leaves cyanuret of silver. (LIEBIG.)

COBALTO-CYANURET OF SILVER is a white crystalline precipitate, formed by mixing solutions of cobalto-cyanuret of potassium and nitrate of silver. It dissolves in ammonia, with which it forms a double compound, crystallizing in colourless transparent prisms.

ARSENITE OF SILVER is precipitated in the form of a very pale yellow powder, soon becoming deeper yellow, gray, and brown, by the addition of solution of arsenious acid to nitrate of silver. Nitrate of silver has already been adverted to as a test for white arsenic (p. 897).

ARSENATE OF SILVER is thrown down from nitrate of silver by arsenic acid, of a reddish-brown colour. At a red heat, this compound evolves oxygen and arsenious acid, and arsenical silver remains. The formula of this salt is $11(ag + O) + (ar + 24O)$.

MOLYBDATE OF SILVER and **TUNGSTATE OF SILVER** are precipitated in the form of white powder, insoluble in water.

CHROMATE OF SILVER is precipitated of a crimson-colour by adding chromate of soda to nitrate of silver. It soon loses its brilliant tint and becomes brown. It is insoluble in cold, and very little soluble in hot water: it is slightly soluble in nitric acid: hydrochloric acid decomposes it, and forms chloride of silver: heat resolves it into oxide of chrome and metallic silver. It forms a double salt with ammonia. It dissolves in nitric acid.

ANTIMONIATE, TELLURATE, and COLUMBATE OF SILVER, are insoluble white powders.

ALLOYS OF SILVER.—The compounds of silver with *potassium*, *sodium*, and the other light metals, have not been examined; neither has it been alloyed with *manganese*. It unites difficultly with *iron*. Upon fusing silver with iron, the alloy separates into silver retaining about one-thirtieth of iron, and iron retaining about one-eightieth of silver; the latter has a peculiar hard and crystalline texture. (MORVEAU, *Journ. de Phys.*, 1788.) When silver and *steel* are fused together, an alloy is formed, which appears perfect while in fusion, but globules of silver exude from it on cooling, which shows the weak attraction of the metals. At a very high temperature the greater part of the silver evaporates, but a portion equal to about 1 in 500 remains, forming a perfect alloy, admirably adapted to the formation of cutting instruments. (STODART and FARADAY, *Quarterly Journal*, ix.) Silver readily combines with *zinc*, producing a brittle bluish-white granular alloy. When an alloy of 11 of zinc and 1 of silver is highly heated in an open crucible, it burns, and the whole of the silver is sublimed with the oxide of zinc. With *tin* silver forms a white hard brittle alloy. Silver made standard by tin is brittle, and does not ring well. (HATCHETT, *Phil. Trans.*, 1803.) The alloy with *cadmium* has not been described. When *cobalt* and silver are fused together, the metals separate on cooling, each retaining a small portion of the other; the silver is rendered brittle, and the cobalt white. (GELLERT.) The alloy of silver and *nickel* has not been examined. The alloy with *copper* constitutes plate and coin*: by the addition of a small proportion of copper to silver, the metal is rendered harder and more sonorous, while its colour is scarcely impaired. Even with equal weights of the two metals, the compound is white: the maximum of hardness is obtained when the copper amounts to one-fifth of the silver. The *standard silver* of this country consists of $11\frac{2}{10}$ pure silver and $\frac{1}{10}$ copper, or 11·10 silver and 0·90 copper. A pound troy, therefore, is composed of 11 oz. 2 dwts. pure silver, and 18 dwts. of copper. Its density is 10·3; its calculated density is

* TABLE of the Weight, Value, &c. of BRITISH SILVER COIN.

Number of pieces in the lb. troy.	Standard weight of each piece.		Fine silver in each piece.		Allowance for the current wear.	Remedy by Indenture 16 Aug. 1817, above or below Standard.		Working remedy for the Moneyers by Mint Regulation.						Legal tender.	Standard weight in troy grains.
						Weight	Finesses	On each piece above or below Stand.	Heaviest piece.		Lightest piece.				
792 Pence . .	dt.	gr.	dt.	gr.	Allowed to pass current without any limitation as to weight.	dwt.	dwt.	gr.	dt.	gr.	dt.	gr.	40s.	gr.	
						1	1	·03							7·272
396 Twopences .		14·54		13·45		·06		14·60		14·48			14·545
264 Threepences .		21·81		20 18		·09		21·90		21·72			21·818
198 Fourpences .	1	5·09	1	2·90		·12	1	5·21	1	4·97			29·090
132 Sixpences .	1	19·63	1	16·36		·18	1	19·81	1	19·45			43·636
66 Shillings .	3	15·27	3	8·72		·36	3	15·63	3	14·90			87·272
26 & 1 Sh. } ½-Crowns .	9	2·18	8	9·81	·90	9	3·09	9	1·27		218·181		
13 & 1 Sh. } Crowns .	18	4·36	16	19·63	1·81	18	5·18	18	2·54		436·363		

The assays of silver are reported in ounces and dwts. the lowest is $\frac{1}{4}$ dwts.
Deliveries of Coin are made by the moneyers, to the Mint office, in journey-weights, each journey = 60 lbs. troy, in value £198.

10·5; so that the metals dilate a little on combining. The French silver coin is constituted of 9 silver and 1 copper; the silver coins of the ancients, and many Oriental silver coins, are nearly pure; they only contain traces of copper and of gold. When silver alloyed by copper, such as standard silver, is exposed to a red heat in the air, it becomes black from the formation of a superficial film of oxide of copper; this may be removed by immersion in hot diluted sulphuric acid, and a film of pure silver then remains, of a beautiful whiteness: this is called *blanched* or *dead silver*; the blanks for coin are treated in this way before they are struck, whence the whiteness of new coin, and the darker appearance of the projecting portions occasioned by wear, in consequence of the alloy showing itself beneath the pure surface; articles of plate are often deadened, or *matted*, by boiling in bisulphate of potassa (*sal enixum*), which acts in the same way as the dilute sulphuric acid. French standard silver is an alloy of 9 of silver and 1 of copper. Lead and silver form a very brittle dull-coloured alloy, from which the lead is easily separated by cupellation (p. 840). When fused lead containing silver is suffered to cool slowly, the lead which first concretes forms granular crystals and is nearly pure, while almost the whole of the silver is contained in the liquid portion: in this way the separation of the two metals may to a certain extent be effected, especially upon the large scale. Antimony forms a brittle white alloy, the density of which exceeds the mean of its components; the greater part of the antimony evaporates during protracted fusion, and the whole may be separated, in the form of oxide, by roasting. There is a rare ore found in Spain, and Suabia, (*antimonial silver*), which has a white metallic lustre, and contains 77 per cent. of silver, and 23 of antimony; its density is 9·82. Bismuth and silver may be combined by fusion; the alloy is brittle, yellow-white, and lamellar; its density exceeds the mean; the density of an alloy of equal weights of bismuth and silver is 10·7. The alloys with *uranium*, *titanium*, *cerium*, and *tellurium*, are not known. When silver and arsenic are fused together, an alloy is formed, composed of 100 silver + 16 arsenic. (GEHLEN.) It is gray, brittle, granular, and by long fusion great part of the arsenic evaporates; it may be entirely got rid of by roasting. Arsenuret of silver is found *native*. 4 parts of silver and 2 of *molybdenum* were strongly heated, but did not yield a button; by continuing the heat a portion of the silver eliquated, still retaining a part of the molybdenum, and becoming bluish when heated: the residuum being again melted in charcoal became more compact, was brittle, gray, and granular. (THOMSON.) The alloys of *chromium* and *vanadium* are unknown. 100 parts of silver and 50 of *tungstic acid*, strongly heated with charcoal, gave a brown button, slightly malleable, weighing 142 grains. (THOMSON.) Silver amalgamates easily with *mercury*: when red hot silver is thrown into heated mercury it dissolves, and when 8 parts of mercury and 1 of silver are thus combined, a granular crystalline soft amalgam is obtained, the density of which exceeds the mean of its components; when a solution of this amalgam in liquid mercury is squeezed through chamois leather, the excess of mercury, retaining only a trace of silver, goes through, and the solid amalgam is left behind. This amalgam exists *native* in octoëdral and dodecaëdral crystals, containing 34·65 per cent. of mercury. Amalgam of silver is sometimes employed for *plating*; it is applied to the surface of copper, and the mercury being evaporated by heat, the

remaining silver is burnished. The better kind of plating, however, is performed by the application of a plate of silver to the surface of the copper, which is afterwards beaten or drawn out. A mixture of chloride of silver, chalk, and pearlash, is employed for silvering brass: the metal is rendered very clean, and the above mixture, moistened with water, rubbed upon its surface. Plating by metallic precipitation from an ammonio-chloride of silver, and also by voltaic precipitation, is now coming into use.

ASSAY OF SILVER.—The analysis of alloyed silver is a very important process, and in continual practice by refiners and assayers. It may be performed in the humid way by dissolving the alloy in nitric acid, precipitating with hydrochloric acid or chloride of sodium, and either reducing the chloride by potassa in the way above described, or estimating the quantity of silver which it contains. The usual method, however, which is employed at the Mint, and by the refiners, is *cupellation**. Of the useful metals, there are three which are capable of resisting the action of air at high temperatures: these are silver, gold, and platinum; the others, under the same circumstances, become oxidized: it might, therefore, be supposed, that an alloy containing one or more of the first three metals, would suffer decomposition by mere exposure to heat and air, and that the oxidizable metal would burn into oxide. This, however, is not the case; for if the proportion of the latter be small, it is protected, as it were, by the former; or, in other cases, a film of infusible oxide coats the fused globule, and prevents the further action of the air. These difficulties are overcome by adding to the alloy some highly-oxidizable metal, the oxide of which is *fusible*. Lead is the metal usually selected for this purpose, though bismuth will also answer. Supposing, therefore, that an *alloy of silver and copper* is to be *assayed*, or analyzed by *cupellation*, the following is the mode of proceeding:—A clean piece of the metal, weighing about 20 grains, is laminated, and accurately weighed in a very sensible balance. It is then wrapped up in the requisite quantity of sheet-lead (*pure*, and reduced from litharge), apportioned by weight to the *quality* of the alloy under examination, and placed upon a small *cupel*, or shallow crucible, made of bone-earth, which has been previously heated. The whole is then placed within the *muffle*, heated to bright-redness: the metals melt, and, by the action of the air which plays over the hot surface, the lead and copper are oxidized and absorbed by the cupel, and, if the operation has been skillfully conducted, a button of pure silver ultimately remains, the completion of the process being judged of by the cessation of the oxidation and motion upon the surface of the globule, and by the very brilliant appearance assumed by the silver when the oxidation of its alloy ceases. The button of pure metal is then suffered to cool gradually, and its loss of weight will be equivalent to the weight of the alloy which has been separated by oxidation, a certain allowance being made for a small loss

* Where great accuracy is requisite, the solution of the alloy, and the precipitation of the silver in the state of chloride, is the method that must be followed; but an experienced assayer will arrive at tolerably close results by cupellation, and where, as in the London Mint, many assays are often daily requisite, the

humid process could not be adopted without serious interruption to the business of the establishment. Where, as in the French Mint, only one degree of fineness is to be estimated, the humid process, conducted with the *precautions* described by M. Gay Lussac, and with the aid of his apparatus, is preferable.

of silver, which always occurs, partly by evaporation, and partly carried off with the oxides which are absorbed by the cupel. To perform this process with accuracy, certain precautions are requisite, which can only be learned by practice, so as to enable the operator to gain uniform results. Instructions upon this subject will be found in AIKIN'S *Chemical Dictionary*; in CHILDREN'S *Translation of Thenard on Chemical Analysis*; in VAUQUELIN'S *Manuel de l'Essayeur*; and in DUMAS' *Chim. app. aux Arts*.

CHARACTERS OF THE SALTS OF SILVER.—The soluble salts of silver are recognised by furnishing a white precipitate with hydrochloric acid, and the soluble chlorides, which blackens by exposure to light, and which is readily soluble in ammonia; and by affording metallic silver upon the immersion of a plate of copper. The salts insoluble in water are mostly soluble in liquid ammonia; when heated on charcoal before the blowpipe, they afford a globule of silver. All the salts of silver, excepting those which contain coloured acids, are colourless, provided they have not been exposed to light, or deoxidizing agents, of the influence of which they are extremely susceptible. A yellow precipitate on the addition of phosphate of soda, and of the soluble arsenites, a red-brown by arseniates, a crimson by the chromates, and white by ferrocyanuret of potassium, are further characteristics of the soluble salts of silver.

Tin and lead are the most rapid precipitants of *metallic silver* from the nitrate; cadmium, zinc, copper, bismuth, and antimony, are more slow in their operation, and arsenic and mercury still more tardy. In all cases the silver appears crystallized; often blackish at first, but afterwards assuming the metallic lustre. Iron is a speedy reducer of the sulphate of silver. The insoluble salts of silver mixed with water are also similarly decomposed, but the operation is more slow. Chromate of silver, probably on account of its insolubility, is extremely slowly reduced; cadmium is the most effective metal for the purpose. Chloride of silver is rapidly reduced by most of the metals which form soluble chlorides, such as zinc, iron, cadmium, cobalt, and arsenic; lead, nickel, copper, antimony, and mercury, act slowly; and tin and bismuth are very feeble in their action. Zinc, copper, and arsenic, rapidly deduce the ammoniacal solution of oxide of silver. Of all the metallic precipitants zinc and cadmium are the most effective; but when zinc or antimony are used, the separated silver contains those metals.

§ XXXII. GOLD.

GOLD has been known from the remotest ages; it is the *sol* of the alchemists, and they represented it by the circle ☉, which is also the emblem of perfection. Its chemical history has not been so satisfactorily worked out as that of most of the other metals. The best early authority upon it is Lewis (*Philosophical Commerce of the Arts*), and as regards most of its important alloys, Mr. Hatchett's *Experiments and Observations on the Alloys, Specific Gravity, and Comparative Wear of Gold* (*Phil. Trans.*, 1803), must be consulted.

Gold occurs in nature in a metallic state alloyed with silver or copper, and in this state it is called *native gold*. Its colour is various shades of yellow; it is either massive, ramose, or crystallized in cubes and octoëdra. In these varieties of gold the proportion of silver fluctuates between 8

and 70 per cent. (BOUSSINGAULT.) The veins of gold are confined to primitive countries, but large quantities of this metal are collected in alluvial soils and in the beds of certain rivers, more especially those of the west coast of Africa, and of Peru, Brazil, and Mexico. In Europe, the streams of Hungary and Transylvania have afforded a respectable quantity of gold; it has been found also in the Rhine, the Rhone, and the Danube. Small quantities have been collected in Cornwall, and in the county of Wicklow in Ireland.

Gold may be obtained pure by dissolving 1 part, by weight, of standard gold in 3 of nitrohydrochloric acid, (composed of 1 part, by weight, of nitric, and 2 of hydrochloric acid,) evaporating the solution to dryness, (by a gentle heat towards the end of the process,) redissolving the dry mass in distilled water, filtering, and adding to it a solution of protosulphate of iron; a black powder falls, which after having been washed with dilute hydrochloric acid and distilled water, affords, on fusion with a little borax or other suitable flux, a button of pure gold. For the purpose of solution gold may conveniently be kept in the pulverulent state.

Gold is of a deep and peculiar yellow-colour. It melts at a bright red-heat, equivalent, according to Daniell, to 2016° of Fahrenheit's scale, and when in fusion appears of a brilliant greenish colour: as it solidifies it contracts in bulk, and by very slow cooling was obtained by Tillet and Monge in short quadrangular pyramidal crystals. Its specific gravity is 19.3. Its specific heat is $= 0.03244$. (REGNAULT.) It is so malleable, that it may be extended into leaves which do not exceed one two hundred and eighty-two thousandth of an inch in thickness, or a single grain may be extended over 56 square inches of surface. This extensibility of the metal is well illustrated by gilt buttons, 144 of which are gilt by 5 grains of gold, and less than even half that quantity is adequate to giving them a very thin coating. It is also so ductile that a grain may be drawn out into 500 feet of wire. It shows no tendency to unite to oxygen when exposed to its action in a state of fusion; if an electric discharge be passed through a very fine wire of gold, a purple powder is produced, which has been considered as an oxide, though probably it is only finely-divided gold. The pure acids have no action upon gold; neither has sulphur or sulphuretted hydrogen; chlorine, iodine, bromine, and fluorine? on the contrary, are capable of dissolving it; the agent, commonly resorted to for this purpose is chlorine, generally in the form of nitrohydrochloric acid, or *aqua regia*. The combination of oxide of gold with the alkalis, and the double salts which are thus produced, are also important features in the history of this metal, and have very extensive and interesting applications to the arts; under Mr. Elkington's patent, such solutions are largely used for the purposes of gilding copper and other metals, and have almost entirely superseded the old and pernicious practice of *water gilding*, as it was termed, in which mercury is used as the solvent.

There is considerable difficulty in determining the equivalent of gold, in consequence of the indefinite character of its protocompounds: hence Gmelin adopts the number 66 as its equivalent; Graham 99.6; Thomson 100; and Turner 199.2. Following Dr. Turner in the view which he takes of the atomic constitution of the oxides and chlorides of gold, I have assumed 200 as its equivalent, though Thomson's number is most consistent with that deduced from the specific heat (p. 163).

PROTOXIDE OF GOLD. AUROUS OXIDE. ($au + o$), $Au_2 O$ (GRAHAM), may be obtained by the action of a cold solution of potassa on *protochloride* of gold; the product must be washed with water, and dried at a temperature of 100° ; if the heat exceed this, a portion of the oxide is reduced, and it is converted into peroxide and metallic gold; it is of an olive colour. It is soluble in the alkaline solution, which, therefore, must be sparingly used. It consists of

Gold 1 200 96.15 Berzelius. 96.13
Oxygen 1 8 3.85 3.87
Protoxide of gold	1.	208	100.00	100.00

DEUTOXIDE OF GOLD.—The existence of this step of oxidizement is very doubtful: it is stated to be the product of the combustion of gold by electricity, as when a powerful electric battery is discharged through a fine wire or leaf of gold: in these cases it is dissipated into a purple powder, which has been called the *purple oxide of gold*, but it is probably only the metal in a state of very minute division: at all events, we have no experimental evidence to prove that it is an oxide.

PEROXIDE OF GOLD. AURIC OXIDE. AURIC ACID. ($au + 3 o$.) $Au_2 O_3$ (GRAHAM).—According to Pelletier, the best process for obtaining peroxide of gold consists in the decomposition of the *perchloride* by magnesia, washing the precipitate with dilute nitric acid, to remove any excess of the precipitant, and drying it at a very low heat. Dr. Turner, upon the authority of Dr. Wagner of Pesth in Hungary, suggests the following as the most certain process for procuring peroxide of gold. Dissolve 1 part of gold in the usual way, render it neutral by evaporation, and redissolve in 12 parts of water; to the solution add 1 part of carbonate of potassa dissolved in twice its weight of water, and digest at about 170° ; carbonic acid gradually escapes, and the hydrated peroxide, of a brownish-red colour, subsides; after being well washed, it is dissolved in colourless nitric acid of the specific gravity 1.4, and the solution decomposed by admixture with water; the hydrated peroxide is thus obtained quite pure, and is rendered anhydrous by exposure to a temperature of 212° . In this anhydrous state it is nearly black, insoluble in water, and decomposed either by exposure to solar light or by heat. It is soluble in hydrochloric acid, forming the common solution of gold; and it dissolves in sulphuric and in nitric acid, but the affinity is here so weak that the solutions are decomposed by the action of water, and yield no saline compound when evaporated with the utmost caution. These properties led Pelletier to examine the action of alkalis upon this oxide, and he found that, digested in a solution of caustic potassa, it was dissolved; it also combines with baryta; and in these cases apparently plays the part of a weak acid. Boiled with chloride of potassium or sodium, a yellow solution results, which is alkaline, and contains chloride of gold and aurate of potassa or soda. The action of ammonia on chloride of gold will presently be noticed. This oxide consists of

Gold 1 200 89.3 Berzelius. 89.23
Oxygen 3 24 10.7 10.77
Peroxide of gold	1	224	100.0	100.00

PROTOCHLORIDE OF GOLD. ($au + c.$)—When perchloride of gold is placed on a sand-heat in a porcelain capsule, and exposed, under frequent stirring, to the temperature of melting tin till it no longer evolves chlorine, a white saline mass remains, which, unless it contains undecomposed perchloride, is not soluble in water: it may be preserved unchanged whilst dry, but in contact of water it gradually changes into perchloride and metallic gold: this decomposition of the protochloride is instantaneous when boiling water is poured upon it, 2 parts of metallic gold being separated for 1 that is held in solution. It consists of

					Berzelius.	
Gold	1	200	84.75		85	
Chlorine	1	36	15.25		15	
Protochloride of gold	1	236	100.00		100	

PERCHLORIDE OF GOLD. ($au + {}^3c.$)—When gold in a state of minute division is heated in chlorine, a compound of a deep-yellow colour results. Gold-leaf also dissolves easily in a strong aqueous solution of chlorine, and affords a similar compound on evaporation. The common solvent of gold, however, for the purpose of obtaining the chloride, is the nitrohydrochloric acid. By evaporation, the saturated solution affords prismatic crystals of a deep orange-colour, very deliquescent, fusible, and then decomposed by heat, yielding, at first, the protochloride, and ultimately, pure gold. It is said, that, when heated, a very minute portion of the metal also passes off with the chlorine and water. When concentrated sulphuric acid is poured into a strong solution of this compound, it causes a precipitation of *anhydrous chloride of gold*. The colour of its aqueous solution varies; if neutral and concentrated it is nearly red (*Leo ruber* of the alchemists), if dilute, or acid, it is yellow. It has a rough bitterish taste.

The solution of perchloride of gold in hydrochloric acid, (*hydrochlorate of chloride of gold*), or *muriate of gold*, as it is usually called, yields yellow prismatic or acicular crystals on evaporation; its solution is discoloured by steam in the same way, and apparently from the same cause, as nitrate of silver. (See p. 959.) It is decomposed by hydrogen, phosphorus, charcoal, sulphurous acid, and many of the metals; a piece of paper, moistened with it and exposed to light, also becomes purple in consequence of its decomposition. According to Van Mons, it is decomposed by several vegetable acids, and when mixed with binoxalate of potassa, carbonic acid gas is evolved, and the gold gradually separated.

When solution of protosulphate of iron is added to chloride of gold, the mixture instantly acquires a dingy green or brown tinge, and appears of a beautiful green or blue, if viewed by strong transmitted light: these appearances depend upon the presence of an infinite number of small particles of gold in the metallic state; they soon subside in the form of a brown powder which, after having been washed with boiling water, digested in boiling dilute hydrochloric acid, and again washed and dried, is pure gold; in this pulverulent state, it is used for gilding porcelain, and for some other purposes of the arts; the modes of applying it are described by Dumas. (*Chim. app. aux Arts*, iii. 689.) This method of separating gold from its solution is often convenient in analytical operations, and the

gold powder in that case is generally fused into a button with a little borax. According to Dr. Turner, the mutual action of the protosulphate and perchloride is such, that 6 atoms of protosulphate of iron, and 1 of perchloride of gold, produce 2 atoms of persulphate of iron, 1 of perchloride of iron, and 1 of gold.

PURPLE OF CASSIUS.—Protochloride of tin, added to a dilute solution of chloride of gold, occasions an instant change of colour to a reddish-brown or dirty-purple: if a piece of tin-foil be immersed in a dilute solution of the chloride, the same purple powder is presently thrown down upon it; it is also formed when an alloy of 150 parts of silver, 35 of tin, and 20 of gold, is digested in nitric acid; nitrate of silver is dissolved, and the purple powder remains. According to Graham, the finest coloured precipitate is formed "when protochloride of tin is added to a solution of the perchloride of iron till the colour of the liquid has a shade of green, and adding this liquid, drop by drop, to a solution of perchloride of gold, which is free from nitric acid and very dilute; after 24 hours a brown powder is deposited, which is in a small degree transparent, and purple-red by transmitted light; when dried and rubbed to powder, it is of a dull blue colour." (See also DUMAS upon this subject.)

The purple of Cassius is used in enamel and porcelain painting, and also for tinging glass of a fine red colour. It retains its colour at a high red-heat: it is insoluble in solutions of potassa and soda, but if, whilst in its hydrated state, it be washed with ammonia, a bright purple liquid is obtained, from which the colouring matter very slowly precipitates.

The chemical nature of this compound has given rise to much discussion. It would appear, from Proust's experiments, to consist of about 3 parts of oxide of tin, and 1 of protoxide of gold. Oberkampf found the composition and colour of the precipitates formed by protochloride of tin in solutions of gold, liable to much variation. When the tin predominates, it is of a violet colour; but when the gold is in excess, it is more pink; and these colours are also communicated to enamel. Oberkampf and Macar-dieu assert, that the gold in the compound is in the metallic state; that the violet combination contains 60 oxide of tin, and 40 gold, and the pink about 20 and 80 (*Ann. de Ch. et Ph.*, xxx. 147); but as mercury does not abstract gold from it, this view is improbable.

According to Berzelius, the purple of Cassius, when heated to redness, loses between 7 and 8 per cent. of water, and the residue is a mixture of metallic gold and peroxide of tin. He considers it as a compound of protoxide of gold and sesquioxide of tin. (See also GAY LUSSAC, *Ann. de Ch. et Ph.*, xlix.) According to Dr. Turner, the purple of Cassius is a hydrated double salt, composed of peroxide of tin, as the *acid*, united with protoxide of tin and binoxide of gold, as *bases*, in such proportion that the oxygen of the gold exactly suffices to convert the protoxide into peroxide of tin.

When nitrate or sulphate of silver is added to chloride of gold, a precipitate falls, consisting of chloride of silver and oxide of gold; the latter may be removed by hydrochloric acid: the protosalts of mercury are rendered deep-brown, or reddish-brown, by chloride of gold: many organic substances give it a purple tint: it tinges the cuticle of an indeli-

ble purple tint: the readiness with which paper and other organic bodies acquire this hue by exposure to light has led to the use of chloride of gold in some photographic processes.

Chloride of gold dissolves in alcohol, and in ether: the latter solution is generally obtained by agitating the solution of gold with ether, after which the mixture separates into two portions; the superior is yellow, and is an ethereal solution of chloride of gold; the inferior colourless, being only water and hydrochloric acid. This ethereal solution was formerly much esteemed as a medicine, under the name of *aurum potable*; it was presumed that gold might possibly communicate something of its own durability to the human constitution. Polished steel dipped into this solution acquires a coat of gold, and it has hence been employed for gilding delicate cutting instruments. It generally deposits films of metallic gold, sometimes in ramose or arborescent crystals. The perchloride of gold consists of

						Berzelius.
Gold	.	.	.	1	.	200 . . 65 . . 65.09
Chlorine	.	.	.	3	.	108 . . 35 . . 34.91
<hr/>						
Perchloride of gold				1		308 . . 100 . . 100.00

FULMINATING GOLD. AURATE OF AMMONIA. AMMONIURET OF PEROXIDE OF GOLD.—When liquid ammonia is added to a concentrated solution of chloride of gold diluted with about 3 parts of water, a yellowish-brown precipitate is formed, which, if collected upon a filter, washed with a little water, and carefully dried at the temperature of 212° , is *fulminating gold*. A more powerfully fulminating compound is obtained by digesting peroxide of gold in liquid ammonia; it acquires a deep olive colour, and may be dried carefully at 212° , but if suddenly heated to about 290° , it explodes with great violence, and if thus detonated upon platinum leaf, the metal is torn at the point of contact, as is the case with all these exploding combinations: friction with hard bodies, or an electric shock, also explode it; with the exception of the hydrochloric, the acids have little action on this compound. It probably consists of 2 atoms of ammonia, and 1 of peroxide of gold, or is a *diaurate of ammonia*. Dumas regards it as a hydrated nitruet of gold combined with ammonia; but the former is the more simple and probable view of its proximate composition.

AURO-PERCHLORIDES.—Under this term are comprehended the compounds described by Bonsdorff (*Ann. de Ch. et Ph.*, xlv.) and others, in which the chloride of gold is combined with certain electro-positive chlorides, such as those of the alkaline bases: they consist of 1 atom of terchloride of gold, and 1 atom of the other chloride, and may be formed of their respective chlorides in such proportions; some of them have been long known: they mostly form prismatic crystals, and include water of crystallization. It is in consequence of the formation of these soluble double salts, that the solution of chloride of gold in hydrochloric acid yields no precipitates with the alkalis, even when added in excess. Different aurochlorides, obtained by adding salts of potassa, soda, ammonia, and other bases, to the chloride, are employed in gilding copper trinkets, buttons, and other articles, under Mr. Elkington's patent.

AURO-PERCHLORIDE OF AMMONIA is formed by dissolving the component salts in atomic equivalents and evaporating; it crystallizes in efflorescent acicular prisms, soluble in water and alcohol, and containing

Hydrochlorate of ammonia	1	54	13.6
Perchloride of gold	1	308	77.4
Water	4	36	9.0
<hr/>			
Auro-perchloride of ammonia (crystallized)	1	398	100.0

AURO-PERCHLORIDE OF POTASSIUM.—This salt may be obtained by evaporating mixed solutions of chloride of potassium and perchloride of gold in yellow four-sided prisms, slightly efflorescent, and which, dried at 212° , lose their water of crystallization; at a higher temperature chlorine is evolved, and the salt fuses into a dark-brown liquid, which probably contains protochloride of gold, but which water and dilute hydrochloric acid resolve into the original salt, chloride of potassium and metallic gold being separated. The components of the crystallized double chloride are, according to Bonsdorff,

Chloride of potassium	1	76	17.8
Perchloride of gold	1	308	71.7
Water	5	45	10.5
<hr/>			
Crystallized auro-perchloride of potassium	1	429	100.0

AURO-PERCHLORIDE OF SODIUM forms four-sided prisms, permanent in the air, and easily fusible in their water of crystallization; they contain

Chloride of sodium	1	60	14.5
Perchloride of gold	1	308	74.4
Water	5	45	11.1
<hr/>			
Crystallized aurochloride of sodium	1	413	100.0

The *auro-perchlorides of lithium, calcium, barium, strontium, magnesium, manganese, zinc, cadmium, cobalt, and nickel*, have also been examined by Bonsdorff: they form hydrated prismatic salts, generally similar to the preceding.

IODIDE OF GOLD. (*au + i.*)—The action of *iodine* on gold has been examined by Pelletier. (*Quarterly Journal*, x. 121.) When iodide of potassium is added to chloride of gold, it produces a copious yellowish-brown precipitate, insoluble in cold water, and easily decomposed by heat and by the liquid alkalis. When boiled in water, to deprive it of excess of iodine, it consists of

Gold	1	200	61.5	Pelletier.
Iodine	1	126	38.5	34
<hr/>				
Protiodide of gold	1	326	100.0	100

BROMIDE OF GOLD. (*au + b.*)—Bromine combines with gold, and forms a dark-gray substance, soluble in water, and crystallizing from its solution in deep-brown crystals. This salt has so intense a colour, that it communicates a tinge to 5000 parts of water. (BALARD, *Ann. de Ch. et Ph.*, xxxii. 362.)

SULPHURET OF GOLD (*au + 3s*) is procured by passing sulphuretted hydrogen through an aqueous solution of perchloride of gold. It falls in the form of a black powder, easily resolved by heat into metallic gold and sulphur. (OBERKAMPF, *Ann. de Ch.*, lxxx.) It consists of

				Oberkampf.	Buchholz.
Gold	1 . .	200 . .	80.6 . .	80.39 . .	82 . .
Sulphur	3 . .	48 . .	19.4 . .	19.61 . .	18 . .
Persulphuret of gold	1 . .	248 . .	100.0 . .	100.00 . .	100 . .

A double *sulphuret of gold and potassium* is formed when gold, sulphur, and potassa, are fused together; the compound is soluble in water, and acids throw down sulphuret of gold from the solution. This solubility of gold in alkaline sulphurets was known to the old chemists, and it was thus, according to Stahl, that Moses dissolved the golden calf. This compound is used in the potteries as a source of the preparation of gold, with which a dingy gilding is occasionally given to earthenware. (DUMAS.)

PHOSPHURET OF GOLD is obtained by heating gold-leaf with phosphorus, in a tube deprived of air. It is a gray substance of a metallic lustre, and consists probably of 1 proportional of gold and 1 of phosphorus. It is decomposed when heated under exposure to air. When phosphuretted hydrogen is passed through a dilute solution of chloride of gold, a brown powder falls, which is metallic gold; but if the solution of gold be dropped into excess of phosphuretted hydrogen, a phosphuret of gold appears to be produced.

PERCYANURET OF GOLD (*au + cy*) is thrown down as an insoluble pale-yellow compound, by adding cyanuret of potassium to chloride of gold; it forms, according to Ittner, double salts with the cyanurets of the alkaline bases. According to Liebig, this cyanuret is best prepared by adding to a solution of chloride of gold, deprived of free acid, a solution of caustic potassa to which excess of hydrocyanic has been added. Excess of cyanuret of potassium redissolves the precipitate, but it is again thrown down by an acid. Cyanuret of gold is also formed by adding to 16 parts of gold dissolved in nitrohydrochloric acid, a hot solution of 24 parts of cyanuret of mercury, evaporating to dryness, and washing with pure water.

SULPHOCYANURET OF GOLD is a flesh-coloured powder, which falls when solution of sulphocyanuret of potassium is mixed with chloride of gold: it is soluble in the precipitant and in ammonia. (GROTHUSS.)

ALLOYS OF GOLD.—The alloys of gold with *potassium* and *sodium* have not been examined. With *manganese* it forms a gray brittle alloy, hard, somewhat ductile, and of great lustre. Mr. Bingley found the proportion of manganese to form from one-eighth to one-ninth of the compound: it was obtained by heating gold with oxide of manganese which had been repeatedly mixed and burned with olive oil. Cupellation with lead separated the manganese. With *iron* the alloy is malleable and ductile and harder than gold; its colour dull-white, and its specific gravity, when containing 11 gold + 1 iron, 16.885. The metals expand by union; so that, supposing their bulk before combination to have been 1000, after combination it is 1014.7. With *zinc* the compound is brittle and brass-coloured: specific gravity, when containing 11 gold + 1 zinc, 16.937. The metals contract a little in uniting; the original bulk being 1000, that of the alloy is 997. The brittleness continued when the zinc was reduced to one-sixtieth of the alloy. The fumes of zinc in a furnace

containing fused gold, make it brittle; and according to Hellot, when an alloy of 1 of gold and 7 of zinc is ignited in an open crucible, the whole of the gold sublimes with the oxide of zinc. Tin formed a whitish alloy, brittle when thick, but flexible in thin pieces; specific gravity, when constituted of 11 gold + 1 tin, 17·307; bulk before fusion, 1000; after fusion, 981; so that there is considerable contraction. The old chemists called tin, *diabolus metallorum*, from its property of rendering gold brittle; but Mr. Bingley's experiments, quoted by Mr. Hatchett, show that one-sixtieth of tin does not render gold brittle; indeed, Mr. Alchorne's experiments (*Phil. Trans.*, 1784), showed that gold might be rolled and coined, when containing one thirty-seventh of tin. At a cherry-red heat Mr. Bingley found that this alloy became dark coloured, and disintegrated from the loss of the tin. Mercadieu obtained the purple of Cassius by digesting the alloy, rich in tin, in nitric acid: hydrochloric acid dissolves the tin and leaves finely-divided gold. The alloy of gold with *cadmium* has not been examined. Mr. Hatchett obtained a dull-yellow alloy with 11 gold + 1 *cobalt*, the density of which was 17·112. The bulk of the metals before fusion being 1000, became 1001 after fusion. When the cobalt was below one sixty-sixth of the mass, the alloy was somewhat ductile. With gold and *nickel* he obtained a brittle brass-coloured alloy, when in the proportions of 11 to 1. The density of the gold being 19·172 and of the nickel 7·8, that of the alloy was 17·068; and the bulk of the metals before fusion being 1000, was increased after fusion to 1007. With *copper*, gold forms a ductile alloy of a deeper colour, harder, and more fusible than pure gold: this alloy, in the proportion of 11 gold to 1 copper, constitutes *standard gold*; its density is 17·157, being a little below the mean, so that the metals slightly expand on combining. One troy pound of this alloy is coined into $46\frac{2}{4}$ sovereigns, or 20 troy pounds into 934 sovereigns and a half. The pound was formerly coined into 44 guineas and a half. (See next page.) The standard gold of France consists of 9 parts of gold and 1 of copper. The alloy of gold with *lead* is very brittle when that metal only constitutes one 1920th of the alloy: even the fumes of lead destroy the ductility of gold: the specific gravity of an alloy of 11 gold + 1 lead is 18·080; and 1000 parts become 1005. A remarkable fact in respect to this alloy is, that its specific gravity diminishes to a certain extent, as the proportion of lead diminishes, and is at its maximum when the lead amounts only to one 96th part, the quantity of gold remaining the same, and the deficiency being made up with copper: the following table exhibits this:—

Metals.	Grains.	Specific Gravity of Alloy.	Bulk before Union.	Bulk after Union.	Expansion.	Metals.	Grains.	Specific Gravity of Alloy.	Bulk before Union.	Bulk after Union.	Expansion.
Gold ...	442	18·080	1000	1005	5	Gold ...	442	17·032	1000	1035	35
Lead ...	38					Copper ...	34				
						Lead ...	4				
Gold ...	442	17·765	1000	1006	6	Gold ...	442	16·627	1000	1057	57
Copper ...	19					Copper ...	37·5				
Lead ...	19					Lead ...	0·5				
Gold ...	442	17·312	1000	1022	22	Gold ...	442	17·039	1000	1031	31
Copper ...	30					Copper ...	37·75				
Lead ...	8					Lead ...	0·75				

TABLE of the Weights, Value, &c., of BRITISH GOLD COIN.

Number of pieces in the pound weight.	Standard weight of each piece.	Fine gold in each piece.	Current weight of carats, not to pass below.	Allowance for wear.	Remedy by indurture in the lb.		Working remedy for the moneyers, by Mint regulation.			By Mint regulation the Bank must receive, if not heavier than	Legal tender.	Standard weight in troy grains.
					Weight.	Fine ness.	On each piece above or below standard.	Heaviest piece.	Lightest piece.			
178	$\frac{1}{4}$ guineas.	oz. dwt. gr. 0 1 8.35	oz. dwt. gr. 0 1 5.66	gr. 55	gr. 40	gr. 40	gr. 22	oz. dwt. gr. 0 1 8.84	oz. dwt. gr. 0 1 8.134	dwt. gr.		gr. 32.359
133 $\frac{1}{2}$	$\frac{1}{3}$ ditto.	0 1 19.14	0 1 15.55	1.14	"	"	.29	0 1 19.445	0 1 18.846			43.146
89	$\frac{1}{2}$ ditto.	0 2 16.71	0 2 11.32	.71	"	"	.44	0 2 17.168	0 2 16.269			64.719
44 $\frac{1}{2}$	Guineas.	0 5 9.43	0 4 22.65	1.43	"	"	.89	0 5 10.337	0 5 8.539			129.438
22 $\frac{1}{4}$	2 ditto.	0 10 18.87	0 9 21.30	2.87	"	"	1.79	0 10 20.674	0 10 17.078			258.876
9, wanting $\frac{1}{2}$ guinea.	$\frac{1}{2}$ ditto.	1 6 23.19	1 4 17.25	7.19	"	"	4.49	1 7 3.685	1 6 18.697			647.191
93 $\frac{3}{4}$ or 1369 in 20 lbs.	$\frac{1}{2}$ sovereigns.	0 2 13.63	0 2 8.500	$\frac{1}{2}$ = .512	12	15	.128	0 2 13.765	0 2 13.508	$\left\{ \begin{array}{l} 808 = \frac{1}{6} \text{ gr. ab.} \\ 2 \text{ 13} = \frac{1}{6} \text{ Stan.} \end{array} \right.$	To any amount.	61.163
46 $\frac{5}{8}$ or 934 & $\frac{3}{4}$ in 20 lbs.	Sovereigns.	0 5 3.27	0 4 17.001	$\frac{3}{4}$ = .774	"	"	.256	0 5 3.531	0 5 3.017	$\left\{ \begin{array}{l} 607 = \frac{1}{6} \text{ gr. ab.} \\ 5 \text{ 3} = \frac{1}{6} \text{ Stan.} \end{array} \right.$		123.274
23 $\frac{1}{4}$ and $\frac{9}{16}$	£2 pieces.	0 10 6.54	0 9 10.003	1.548	"	"	.513	0 10 7.062	0 10 6.035			246.548
9 and $\frac{69}{100}$	£5 pieces.	1 5 16.37	1 3 13.008	"	"	"	1.284	1 5 17.556	1 5 15.088			616.372

The assays of gold are reported in carats and grains; the lowest is $\frac{1}{6}$ ct. gn. = 7 $\frac{1}{2}$ troy grains.
 Deliveries of coin are made in journey-weights, each journey = 15 lbs. troy, in value £700 17s. 6d.

Gold and *antimony* form a brittle yellow compound: Mr. Hatchett found gold made standard by antimony to be of a pale and dull colour, very brittle and fine-grained, and its density 16·929, the bulk of the metals being reduced by combination from 1000 to 987. When the antimony only formed one 1920th of the mass, it was still brittle, and the fumes of antimony in the neighbourhood of fused gold destroy its ductility. A standard alloy of gold with *bismuth* was brittle, fine grained, and of a greenish-yellow colour: its density 18·038; the bulk of the metals being reduced from 1000 to 988. The colour of the alloy became nearly that of gold when the bismuth formed one 60th, but it remained brittle with only one 1920th: the fumes of bismuth also destroy the ductility of gold which has been fused in the same furnace. *Uranium*, *titanium*, and *cerium*, have not been examined in their relations to gold. The alloy of gold and *tellurium* exists *native*. *Arsenic* and gold are not easily combined, in consequence of the volatility of the former metal. Mr. Hatchett added 453 grains of arsenic to 5307 of fused gold, and having stirred the mixture poured it into an iron mould: only 6 grains were retained, so that the alloy contained one 885th of arsenic; it had the colour of gold, and was brittle: by suspending gold in the fumes of arsenic, he obtained a brittle fusible alloy of a gray colour. *Molybdenum* and gold form a black brittle compound. (HIELM, *Crell's Annals*, iii.) The action of gold and *chromium* has not been examined. Little is known of the compound of gold with *tungsten*: "When 100 parts of gold, 50 of tungstic acid, and a quantity of charcoal-powder, were strongly heated in a covered crucible, complete fusion did not take place; the button weighed 139 grains; by cupellation with lead the gold was reduced to its original purity." *Mercury* and gold combine readily at common temperatures, and more rapidly when heated, the mercury taking up a considerable proportion of gold without loss of fluidity: when rich in gold, the amalgam is of a buttery consistence, and may be separated from the more liquid compound by pressure through leather; it then consists of 2 parts of gold and 1 of mercury: the amalgam used for gilding bronze contains about one eighth of gold. *Silver* and gold appear to combine readily in all proportions, when the fused metals are stirred together; but that there is a tendency to definite combination appears from Homberg's experiments, who kept equal parts of gold and silver in fusion for a quarter of an hour, and found on breaking the crucible that the ingot consisted of two distinct portions; the uppermost being pure silver, and the lowermost, gold, combined with one sixth of silver: the density of this alloy is a little below the mean, and the colour of gold is rendered paler by a twentieth part of silver. All the gold at present coined is alloyed with copper only; previous to the year 1826, the alloy consisted in part of silver, hence the paler colour of the sovereigns and half sovereigns of former coinages: an alloy composed of equal parts of silver and copper furnishes the best addition to gold for the purpose of coinage, and it is to be regretted that this requisite portion of silver is not made part of the *value* of the coin, by which the system of melting down our gold coin for the purpose of extracting its silver would be prevented, and the perfection and facility of coinage ensured. To separate the silver from gold, the alloy is melted with great excess of silver, granulated, and boiled in

sulphuric acid (in vessels of platinum), by which the silver is oxidized and converted into sulphate of silver, and the metallic gold remains in the form of an insoluble black powder, which is afterwards collected, washed, and fused into a button or ingot. In the same way, the small quantity of gold contained in silver coin, which used to pass unheeded, is extracted by sulphuric acid; the recently-coined silver will accordingly be found destitute of those traces of gold which are contained in our coin of a date anterior to 1826, and in Spanish dollars and other foreign silver. When gold and silver are parted by the action of nitric acid, it is necessary, as in the case of sulphuric acid, that the silver should be in great excess; it is otherwise partially protected from the solvent power of the acid. Mr. Johnson, the eminent refiner, tells me that not only are small portions of silver volatilized, or in some way carried off by the nitrous vapour, but that gold may also be detected in the condensed fumes. In his parting furnaces, the nitrous fumes are carried downwards so as to pass through the fire, and traces of the precious metals are found in the cinders or ashes.

ASSAY OF GOLD.—The analysis of most of the alloys of 'gold is performed by cupellation. A triple alloy of gold, silver, and copper, provided there be a sufficiency of silver present, may be analyzed by digesting it in nitric acid, which takes up the silver and copper, and leaves the gold in the form of a black powder, which may be fused into a button; the silver may be thrown down in the state of chloride, by solution of common salt, and the copper precipitated by iron. The *assay of gold* is more complicated than that of silver, in consequence of the double operation which it has to undergo, namely, first cupellation, and then the separation of the silver by the action of nitric acid. The real quantity of gold or silver taken for an assay is very small; whatever it may be, it is called the *assay pound*. The silver assay pound is divided into 12 ounces, and each ounce into penny-weights and half penny-weights. The gold assay pound is subdivided into 24 carats, and each carat into 4 carat grains, quarters, and eighths. (AIKIN'S *Dictionary*, Art. ASSAY. See also the authorities above quoted, under the Assay of Silver.)

CHARACTERS OF THE SALTS OF GOLD.—It will be observed from the preceding account, that there are, strictly speaking, no oxysalts of gold (the fulminate only excepted?), but that it forms haloid combinations, which are easily decomposed and reduced by heat; such of these as are soluble, are recognised by the peculiar precipitates which they afford with protochloride of tin and protosulphate of iron, and by a black precipitate with protonitrate of mercury. Gold is precipitated in the metallic state from its chloride, or hydrochloric solution, by the greater number of the metals: iron, copper, zinc, and tin, rapidly effect this reduction; lead, mercury, and antimony, more slowly; the tardiness of action is sometimes caused by the adhesion of a film of gold to the precipitating metal. When silver is used, the production of its chloride also impedes the effect: and the same happens with palladium. The gold is generally separated in the form of a brown powder; but copper, iron, zinc, and cadmium, occasion the appearance of a metallic film: and bismuth, antimony, arsenic, and palladium, become coated with a brilliant covering. Tin, after the

separation of a part of the gold, forms the purple of Cassius. Messrs. Elkington's process for gilding by immersing the metals into a hot solution of certain aurochlorides, has been above mentioned; they have also patented a process for gilding by electrochemical action.

§ XXXIII. PLATINUM.

THIS metal was first made known in Europe by Mr. Charles Wood, who met with its ore in the West Indies, in 1741, and sent specimens of it to Dr. Brownrigg, which he afterwards presented to the Royal Society. In 1750, a paper was published upon it by Mr. Wood (*Phil. Trans.*), and by Dr. Lewis, in 1754. In 1752 a dissertation upon it was published by Scheffer, of Sweden; and in 1757 by Margraaf. (*Mém. Berlin.*) The labours of later experimentalists in reference to this metal, I shall presently have occasion to quote. Its name is a diminutive of the Spanish word *plata*, silver.

Platinum is found in the metallic state, in small grains, in South America, confined to alluvial strata, chiefly in Brazil and Peru. It has also been found in the province of Antioquia, in North America; and in considerable quantities in the Uralian mountains of Siberia. (*Edin. Quart. Jour. of Science*, v. 323.) The grains, besides platinum, contain generally gold, iron, lead, palladium, rhodium, iridium, and osmium, and often oxide of titanium and chromate of iron. Rounded masses of the metal, however, occasionally occur among them, and are met with in mineral collections; these are rarely larger than a small marble, though some have been found of the size of a pigeon's egg and upwards. Bous-singault has discovered veins of platinum in the sienitic rocks of Santa Rosa, in the province of Antioquia. (*Ann. de Ch. et Ph.*, xxxii.)

The following details respecting the mode of purifying crude platinum, and rendering it malleable, are taken from Dr. Wollaston's latest paper upon this subject published in the *Philosophical Transactions* for 1829.

"The usual method of giving chemical purity to this metal, by solution in aqua regia and precipitation with sal-ammoniac, are known to every chemist; but I doubt whether sufficient care is usually taken to avoid dissolving the iridium contained in the ore, by due dilution of the solvent. In an account which I gave in the *Philosophical Transactions* for 1804, of a new metal, Rhodium, contained in crude platina, I have mentioned this precaution, but omitted to state to what degree the acids should be diluted. I now, therefore, recommend, that to every measure of the strongest muriatic acid employed, there be added an equal measure of water; and, that the nitric acid used be what is called 'single aquafortis;' as well for the sake of obtaining a purer result, as of economy in the purchase of nitric acid. With regard to the proportions in which the acids are to be used, I may say, in round numbers, that muriatic acid, equivalent to 150 marble, together with nitric acid equivalent to 40 marble, will take 100 of crude platinum; but in order to avoid waste, and render the solution purer, there should be in the menstruum a redundancy of 20 per cent. at least of the ore. The acids should be allowed to digest three or four days, with a heat gradually raised. The solution, being then poured off, should stand until a quantity of fine pulverulent

ore of iridium, suspended in the liquid, has subsided; and should then be mixed with 41 parts of sal-ammoniac, dissolved in about five times their weight of water. The first precipitate, which will thus be obtained, will weigh about 165 parts, and will yield about 66 parts of pure platinum. As the mother-liquor will still contain about 11 parts of platinum, these, with some of the other metals yet held in solution, are to be recovered, by precipitation from the liquor with clean bars of iron, and the precipitate is to be redissolved in a proportionate quantity of aqua regia, similar in its composition to that above directed: but in this case, before adding sal-ammoniac, about 1 part by measure of strong muriatic acid should be mixed with 32 parts by measure of the nitromuriatic solution, to prevent any precipitation of palladium or lead along with the ammoniomuriate of platinum. The yellow precipitate must be well washed, in order to free it from the various impurities which are known to be contained in the complicated ore in question; and must ultimately be well pressed, in order to remove the last remnant of the washings. It is next to be heated, with the utmost caution, in a black-lead pot, with so low a heat as just to expel the whole of the sal-ammoniac, and to occasion the particles of platinum to cohere as little as possible; for on this depends the ultimate ductility of the product.

"The gray product of the platinum, when turned out of the crucible, if prepared with due caution, will be found lightly coherent, and must then be rubbed between the hands of the operator, in order to procure, by the gentlest means, as much as can possibly be so obtained of metallic powder, so fine as to pass through a fine lawn sieve. The coarser parts are then to be ground in a wooden bowl with a wooden pestle, but on no account with any harder material capable of burnishing the particles of platinum; since every degree of burnishing will prevent the particles from cohering in the further stages of the process. Since the whole will require to be well washed in clean water, the operator, in the later stages of grinding, will find his work facilitated by the addition of water, in order to remove the finer portions as soon as they are sufficiently reduced to be suspended in it.

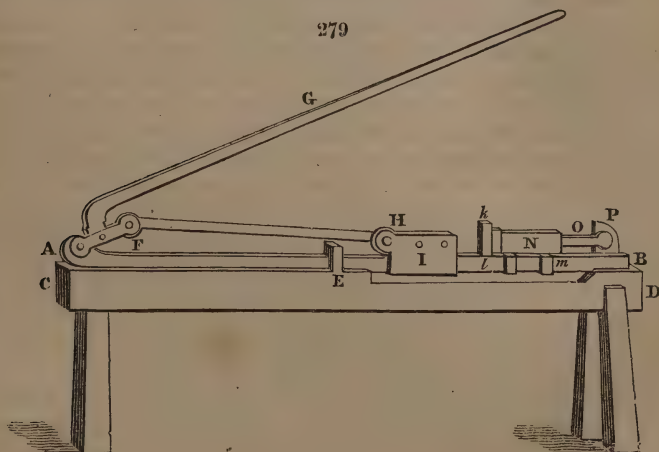
"Those who would view this subject scientifically should here consider, that as platinum cannot be fused by the utmost heat of our furnaces, and consequently cannot be freed, like other metals, from its impurities, during igneous fusion, by fluxes, nor be rendered homogeneous by liquifaction, the mechanical diffusion through water should here be made to answer, as far as may be, the purposes of melting; in allowing earthy matters to come to the surface by their superior lightness, and in making the solvent powers of water effect, as far as possible, the purifying powers of borax and other fluxes in removing soluble oxides.

"By repeated washing, shaking, and decanting, the finer parts of the gray powder of platinum may be obtained as pure as other metals are rendered by the various processes of ordinary metallurgy; and, if now poured over, and allowed to subside in a clean basin, a uniform mud or pulp will be obtained, ready for the further process of casting.

"The mould which I have used for casting is a brass barrel $6\frac{3}{4}$ inches long, turned rather taper within, with a view to facilitate the extraction of the ingot to be formed, being 1.12 inches in diameter at top, and 1.23

inches at a quarter of an inch from the bottom, and plugged at its larger extremity with a stopper of steel, that enters the barrel to the depth of a quarter of an inch. The inside of the mould being now well greased with a little lard, and the stopper being fitted tight into the barrel by surrounding it with blotting-paper, (for the paper facilitates the extraction of the stopper, and allows the escape of water during compression,) the barrel is to be set upright in a jug of water, and is itself to be filled with that fluid. It is next to be filled quite full with the mud of platinum; which, subsiding to the bottom of the water, is sure to fill the barrel without cavities, and with uniformity,—a uniformity to be rendered perfect by subsequent pressure. In order, however, to guard effectually against cavities, the barrel may be weighed after filling it, and the actual weight of its contents being thus ascertained, may be compared with that weight of platinum and water which it is known by estimate that the barrel ought to contain. A circular piece of soft paper first, and then of woollen cloth, being laid upon the surface, allow the water to pass, during partial compression by the force of the hand with a wooden plug. A circular plate of copper is then placed upon the top, and thus sufficient consistency is given to the contents to allow of the barrel being laid horizontally in a forcible press.

“The press which I have generally used for this purpose consists of a flat iron bar *A B*, set edgeways, and screwed down by a hook *E*, near its middle, where it would otherwise be liable to bend, to a strong wooden bench *C D*. The bar is connected by a pivot at its extremity *A*, with the lever *A F G*. An iron rod *F H*, which turns at its two extremities upon the pivots *F* and *H*, proceeds from the lever at *F*, and, as the lever descends, propels forward the carriage *I*, which slides along the bar. A stopper or block being placed in the vacant space *I k*, the carriage communicates motion to the cradle *k l m*, which is also made to slide along the bar, and carries the barrel *N*, which lies upon the cradle, straight against the piston *O*, which rests by its end against *P*, a projection in the further extremity of the bar.



"The weight, which in this machine, when the angle of the lever's elevation is small, will keep the power, applied vertically at the extremity of the lever, *in equilibrio* = that power $\times \frac{AG \times FH}{AF[AF + FH]}$ $\times \cotan.$

of the angle of the lever's elevation; which expression, in the case of the press actually used, becomes, power $\times 5 \cotan.$ of the angle of the lever's elevation. This expression, at an elevation of 5° , becomes nearly $60 \times$ power, and at an elevation of 10° becomes nearly $300 \times$ power; and when the lever becomes horizontal, the multiplier of the power becomes *quasi* infinite. This explanation will be sufficient to show the mechanical advantage with which, by means of this press, the weight of the operator, acting on the end of the lever, will be made to bear against the area of the section of the barrel, a circle little more than an inch in diameter. After compression, which is to be carried to the utmost limit possible, the stopper at the extremity being taken out, the cake of platinum will easily be removed, owing to the conical form of the barrel; and being now so hard and firm that it may be handled without danger of breaking, it is to be placed upon a charcoal fire, and there heated to redness, in order to drive off moisture, burn off grease, and give to it a firmer degree of cohesion. It is next to be heated in a wind-furnace; and for this purpose is to be raised upon an earthen stand about $2\frac{1}{2}$ inches above the grate of the furnace, the stand being strown over with a layer of clean quartzose sand, on which the cake is to be placed, standing upright on one of its ends. It is then to be covered with an inverted cylindrical pot, of the most refractory crucible-ware, resting at its open end upon the layer of sand; and care is to be taken that the sides of the pot do not touch the cake. To prevent the blistering of the platinum by heat, which is the usual defect of this metal in its manufactured state, it is essential to expose the cake to the most intense heat that a wind-furnace can be made to receive, more intense than the platina can well be required to bear under any subsequent treatment; so that all impurities may be totally driven off, which any lower temperature might otherwise render volatile. The furnace is to be fed with Staffordshire coke, and the action of the fire is to be continued for about twenty minutes from the time of lighting it, a breathing heat being maintained during the last four or five minutes. The cake is now to be removed from the furnace, and being placed upright upon an anvil, is to be struck, while hot, on the top, with a heavy hammer, so as at one heating effectually to close the metal. If in this process of forging the cylinder should become bent, it should on no account be hammered on the side, by which treatment it would be cracked irremediably; but must be straightened by blows upon the extremities, dexterously directed, so as to reduce to a straight line the parts which project.

"The work of the operator is now so far complete, that the ingot of platinum may be reduced, by the process of heating and forging, like that of any other metal, to any form that may be required. After forging, the ingot is to be cleaned from the ferruginous scales which its surface is apt to contract in the fire, by smearing over its surface with a moistened mixture of equal parts by measure of crystallized borax and common salt of tartar, which, when in fusion, is a ready-solvent of such impurities,

and then exposing it, upon a platina-tray, under an inverted pot, to the heat of a wind-furnace*. The ingot, on being taken out of the furnace, is immediately to be plunged into dilute sulphuric acid, which in the course of a few hours will entirely dissolve the flux adhering to the surface. The ingot may then be flattened into leaf, drawn into wire, or submitted to any of the processes of which the most ductile metals are capable.

"The perfection of the methods above described, for giving to platinum complete malleability, will best be estimated by comparing the metal thus obtained, in respect of its specific gravity, with platinum which has undergone complete fusion; and by comparing it, in respect of its tenacity, with other metals possessing that quality in the greatest perfection. The specific gravity of platinum, drawn into fine wire, from a button which had been completely fused by the late Dr. E. D. Clarke, with an oxy-hydrogen blowpipe, I found to be 21.16. The aggregate specific gravity of the cake of metallic mud, when first introduced into the barrel, exclusively of moisture, is about 4.3; when taken from the press it is about 10. That of the cake fully contracted, on being taken out of the wind-furnace before forging, is from 17 to 17.7. The mean specific gravity of the platinum, after forging, is about 21.25, although that of some rods, after being drawn, is 21.4; but that of fine platinum-wire, determined by comparing the weight of a given length of it with the weight of an equal length of gold-wire drawn through the same hole, I find to be 21.5, which is the maximum specific gravity that we can well expect to be given to platinum.

"The mean tenacity, determined by the weights required to break them, of two fine platinum-wires, the one of $\frac{1}{3000}$, the other of $\frac{1}{3850}$ of an inch in diameter, reduced to the standard of a wire $\frac{1}{10}$ of an inch in diameter, I found to be 409 pounds; and the mean tenacity of eleven wires, beginning with $\frac{1}{4500}$ and ending with $\frac{1}{25000}$ of an inch, reduced to the former standard, I found to be 589 pounds; the maximum of these eleven cases being 645 pounds, and the minimum 480 pounds. The coarsest and the finest wire which I tried present exceptions, since a wire of $\frac{1}{1500}$ of an inch gave 290 pounds, and a wire of $\frac{1}{30000}$ of an inch, 190 pounds. If we take 590 pounds, as determined by the eleven consecutive trials, to be the measure of the tenacity of the platinum prepared by the process above described, and consider that the tenacity of gold-wire, reduced to the same standard, is about 500, and that of iron-wire 600, we shall have full reason to be satisfied with the processes above detailed, by which platinum has been rendered malleable†."

* "The chemist will find this flux very serviceable for removing from his crucible or other vessels of platinum those ferruginous scales with which, after long use, and particularly after being strongly heated in a coal or coke fire, they become incrustated. In the analysis of earthy minerals, I have been in the habit of using a similar flux, composed of two parts by weight of crystallized carbonate of soda, and one of crystallized borax, well ground together. It has the advan-

tage of not acting, like caustic alkali, upon the platinum crucible, and is a powerful solvent of jargon and many other minerals, which yield with difficulty to other fluxes. If the mineral to be operated on requires oxidation, in order to decompose it, a little nitre or nitrate of soda may be added."

† The method followed in Paris for obtaining pure platinum is described by Baruel. (*Quart. Jour. of Science*, xii.)

The specific heat of platinum, as determined by Regnault, is 0.03243. Its colour is between that of iron and silver: its extreme difficulty of fusion, and the perfect manner in which it resists the action of almost all acids even at a boiling or even red heat, render it importantly useful in many of the arts, and indispensable for various purposes in the chemical laboratory. The curious action of clean surfaces of platinum, and of *spongy platinum*, and of *black platinum* (see *chloride of platinum*), upon gaseous mixtures, and especially in determining the combination of oxygen and hydrogen (p. 386), has also rendered it useful in gaseous analyses, and seems likely to lead to other applications. A piece of paper, dipped into solution of chloride of platinum, dried and burned, yields an ash which exhibits the properties of finely-divided platinum in perfection.

Although platinum is infusible in the highest heat of a furnace, it softens so as to admit of welding and forging as above stated; but in the arc of flame of the voltaic current, and before the oxyhydrogen blowpipe, it admits of being fused even in considerable masses, and when very intensely heated it boils and evaporates, and thin filaments of it scintillate and appear to burn. Dumas states that platinum may be fused in contact with charcoal, but that it then becomes harsh and brittle by combination with a little silicium.

Although pure platinum is insoluble in nitric acid, yet when alloyed with certain other metals soluble in that acid, it is taken up; as for instance, with silver. It is attacked at high temperatures by the alkalis, especially by lithia and potassa, and also by nitre and the alkaline persulphurets: it is not affected by sulphur unless in the spongy or finely-divided state, but it combines with the greater number of the metals, and with many of them forms very fusible compounds; these actions will be presently particularly considered; they show the necessity of caution as to the substances which are ignited or fused in platinum crucibles, and as to the fuel with which they are brought into contact.

The determination of the equivalent of platinum is open to the same difficulties as that of gold. I have adopted 99, which will be found sufficiently consistent with the analytical results which I shall quote. Dr. Turner, upon the authority of Berzelius, assumes 98.8, and L. Gmelin employs the lower equivalent, 48. The number 99 nearly agrees with the deduction from its specific heat (p. 163).

PLATINUM AND OXYGEN.—The affinity of this metal for oxygen is like that of gold, extremely feeble; it shows no disposition to become an oxide, by exposure to air or oxygen at any temperature; and although a strong electric discharge, when transmitted through a fine platinum-wire, dissipates it into black dust, this, as in the analogous case of gold, is probably finely-divided metal, and not the result of combustion or oxidizement. Four definite oxides of platinum are supposed to exist, but of these only two can be satisfactorily identified.

SUBOXIDE OF PLATINUM. ($2\text{ pla} + \text{o.}$)—When nitrate of mercury is added to a dilute solution of perchloride of platinum, a powder falls, which, when carefully heated, gives off calomel, and leaves a *black oxide*

of *platinum*, composed, according to Cooper, of 100 platinum + 4.5 oxygen. (*Journal of Science and the Arts*, vol. iii.) It forms the base of an excellent black enamel.

PROTOXIDE OF PLATINUM. (*pla + o.*)—When protochloride of platinum is gently heated in a solution of caustic potassa, a black oxide is formed, part of which is dissolved by the alkali, and part precipitated: it may be thrown down from its alkaline solution, which is green, or black if concentrated, by dilute sulphuric acid. Heated in a retort, it is reduced, with the escape of water and oxygen gas. It slowly dissolves in the acids, most of which decompose it and resolve it into peroxide and metal: its solutions are not precipitated by sal-ammoniac. Concentrated hydrochloric acid is its best solvent. According to Berzelius, this is the *protoxide*, and consists of

				Berzelius.
Platinum	1	99	92.35	92.40
Oxygen	1	8	7.65	7.60
Protoxide of platinum	1	107	100.00	100.00

SESQUIOXIDE OF PLATINUM. (*pla + 1½ o.*)—When sulphate of platinum is decomposed by ammonia, and the precipitate boiled in weak solution of potassa and cautiously dried, it constitutes *fulminating platinum*: when this is digested in nitric acid a gray powder remains, composed of 100 platinum, 11.86 oxygen. (E. DAVY, *Phil. Trans.*, 1820.) When spongy platinum is heated to redness in an open vessel with caustic potassa, and the product, when cold, washed with water, a gray powder is obtained, which is partly dissolved by the alkali: the residue, washed with dilute nitric acid, and afterwards with water, is also supposed to be *sesquioxide* of platinum, consisting of

				E. Davy.
Platinum	1	99	89.2	89.5
Oxygen	1½	12	10.8	10.5
Sesquioxide of platinum	1	111	100.0	100.0

PEROXIDE OF PLATINUM. (*pla + 2 o.*)—When sulphuret of platinum is digested in nitric acid, and carefully evaporated, or when perchloride of platinum is gently heated in sulphuric acid, a dark-brown solution of *persulphate of platinum* is obtained: if this solution be mixed with nitrate of baryta, sulphate of baryta is thrown down, and pernitrate of platinum remains dissolved; this may be in part decomposed by solution of caustic soda, which forms a yellow precipitate, becoming brown when carefully washed and dried, and which is a *hydrated peroxide*. Heated in a retort, it first gives out water and becomes black; at a higher temperature it evolves oxygen, and the metal is reduced: it has a very feeble attraction for the acids, but readily combines with many of the salifiable bases; it dissolves in the caustic and carbonated alkalis, and may be combined with lime, strontia, and baryta, by adding those earths to its acid solution, when it falls in union with them in the form of a yellow powder. (BERZELIUS.) It forms a fulminating ammoniacal compound, similar to fulminating gold. This oxide consists of

				Berzelius.	Chenevix.
Platinum	1	99	86	85·87	87
Oxygen	2	16	14	14·13	13
Peroxide of platinum	1	115	100	100·00	100

PROTOCHLORIDE OF PLATINUM. (*pla + c.*)—When perchloride of platinum is exposed in a porcelain capsule to a temperature not exceeding that of melting tin, and stirred as long as it evolves chlorine, it is converted into a gray powder, insoluble in water, and not decomposed by sulphuric or nitric acids. It dissolves in boiling hydrochloric acid, and is decomposed, as above stated, by caustic alkali, which separates protoxide. It is decomposed at a red heat, and only gives out chlorine, without a trace of water. It consists of

				Berzelius.
Platinum	1	99	73·4	73·3
Chlorine	1	36	26·6	26·7
Protochloride of platinum	1	135	100·0	100·0

When alcohol is gradually added to a hot concentrated solution of protochloride of platinum in liquid potassa, effervescence ensues from the escape of carbonic acid, and a black powder falls, which, boiled successively with small portions of alcohol, then with hydrochloric acid, and then with potassa, and lastly with repeated portions of water, is Liebig's *platinum black*: it must be separated by decantation, and dried in a porcelain capsule to avoid contact of organic matter. It is metallic platinum in a state of extreme comminution; it may be heated to redness without change of appearance, but at a white heat it assumes metallic lustre; it becomes incandescent when moistened with alcohol, oxygen is absorbed, and acetic acid formed; it immediately inflames a current of hydrogen in the contact of air; it absorbs about 750 times its volume of hydrogen, and also absorbs and retains other gaseous bodies.

When excess of ammonia is added to the hydrochloric solution of protochloride of platinum, and the mixture boiled, it becomes turbid, and deposits deep-green acicular crystals, insoluble in water and in hydrochloric acid, which consists of 1 atom of protochloride of platinum and 1 of ammonia (*pla + c + A*). (MAGNUS.) This salt is not affected by boiling caustic alkalis, nor by boiling sulphuric or hydrochloric acid; so that, as Gros observes, it is difficult to admit that it contains "ammonia in the state of ammonia." When it is digested in hot nitric acid it is converted into a white granular crystalline powder, easily soluble in water, and half the platinum of the green salt is at the same time separated in its metallic state. Neither the chlorine nor the platinum of this nitric salt can be detected by the usual tests: its elements are 1 atom of protochloride of platinum, 2 of ammonia, 1 of oxygen, and 1 of nitric acid, so that its ultimate elements are (*pla + c + 3n + 6o + 6h*). When a hot saturated solution of this nitric salt is mixed with sulphate of soda, the nitric acid is displaced by the sulphuric, and a corresponding sulphate obtained; and a hydrochlorate, phosphate, oxalate, &c. may be similarly obtained by double decomposition. These salts are represented by Gros as containing a compound base, which he compares to ammonium, represented by (*pla + c + 2n + 3h*) = B. The *nitrate* will then be (B + O + n'), the *sulphate* (B + O + s'), and the *hydrochlorate* (B + c), &c. (*Ann. de Ch. et Ph.*, Lxix. 204.)

PERCHLORIDE OF PLATINUM. BICHLORIDE OF PLATINUM. ($pla + 2c$).—When the solution of pure platinum in nitrohydrochloric acid is evaporated, it affords a deep-brown liquid, which shoots into prismatic crystals, consisting of hydrated perchloride of platinum and hydrochloric acid; on further evaporation it yields a brown saline mass, which becomes deeper coloured upon the expulsion of its combined water. It is then a *perchloride of platinum*, yielding a deep-yellow solution in water, and easily soluble in alcohol and in ether. The alcoholic solution is a useful re-agent to detect the presence of potassa: the salt, the base of which is to be ascertained, is first heated to expel ammonia, in case any should be present; it is then dissolved in the smallest possible quantity of water, and mixed with the alcoholic solution of the perchloride: if it be potassa, a triple salt, insoluble in alcohol, is thrown down; if not, the liquid remains clear. Of this double potassium salt, 100 parts are equivalent to 19·3 of potassa, and to 40·4 of platinum. (BERZELIUS.) Perchloride of platinum consists of

Platinum	1	99	57·8
Chlorine	2	72	42·2
<hr/>					
Perchloride of platinum	1		171		100·0

PLATINO-CHLORIDES.—Both the chlorides of platinum enter into definite combination with the chlorides of the alkaline bases, and form *platino-protochlorides*, and *platino-perchlorides*. (BONSDORFF, *Poggend. Ann.*, xiv. MAGNUS, *Ann. de Ch. et Ph.*, Lxix. 204.)

PLATINO-PROTOCHLORIDE OF AMMONIA ($pla + c$) + ($A + hc$) is obtained by adding an equivalent of sal-ammoniac to 1 of protochloride of platinum, dissolved in hydrochloric acid: it forms deep-red crystals.

PLATINO-PROTOCHLORIDE OF POTASSIUM. ($pla + po + 2c$).—This salt was obtained by Magnus in the form of red anhydrous four-sided prisms, insoluble in alcohol, by evaporating a solution of protochloride of platinum and chloride of potassium in hydrochloric acid. It consists of

Platinum	1	99	46·9	} or {	(Protochloride	1	135	63·9
Potassium	1	40	19·0		of platinum}					
Chlorine	2	72	34·1		Chloride of }	1	76	36·1
							potassium }					
	1		211		100·0			1		211		100·0

PLATINO-PROTOCHLORIDE OF SODIUM, similarly obtained, is not crystallizable, and very soluble in alcohol.

PLATINO-BICHLORIDE OF AMMONIA. AMMONIO-MURIATE OF PLATINUM. ($pla + 2c$) + ($A + hc$).—This is the well-known yellow powder which falls when solutions of perchloride of platinum and sal-ammoniac are mixed. When it is exposed to heat it loses a little water, and a compound of sal-ammoniac and protochloride of platinum is at first formed; the ammonia is ultimately decomposed, and the platinum remains in the peculiar spongy state before referred to. This ammonio-chloride is very sparingly soluble in pure water; rather more so in water acidulated by hydrochloric

acid: insoluble in alcohol. If the solution from which it is precipitated contain iridium or palladium, it has a tawny-red colour; these may be removed by boiling in dilute nitric acid and filtering the red solution whilst hot; as it cools it deposits a red crystalline powder, which is generally a triple salt of iridium, and from which the acid may be poured off for use as before. This double chloride, when carefully dried, contains between 44 and 45 per cent. of platinum: it is a compound of

Platinum . . . 1 . . . 99 . . . 43·2	} Bichloride of platinum	} 1 . . . 171 . . . 75·9
Chlorine . . . 2 . . . 72 . . . 32·4		
Ammonia . . . 1 . . . 17 . . . 7·7	} Hydrochlorate of ammonia	} 1 . . . 54 . . . 24·1
Hydrochloric acid 1 . . . 37 . . . 16·7		
Platinobichloride of ammonia . . . 1 . . . 225 . . . 100·0		

PLATINO-BICHLORIDE OF POTASSIUM. ($pla + 2c$) + ($po + c$).—This salt is thrown down in the form of a yellow powder when solutions of chloride of potassium and of bichloride of platinum are mixed; it is very sparingly soluble in water, and is deposited from its boiling solution in small octoëdral crystals: it is insoluble in alcohol; when heated it evolves chlorine, and leaves a mixture of metallic platinum and chloride of potassium. Its difficult solubility renders bichloride of platinum, as already stated, a useful test of the presence of salts of potassa. It is anhydrous, and contains

Bichloride of platinum . . . 1 . . . 171 . . . 69·5
Chloride of potassium . . . 1 . . . 76 . . . 30·5
Platino-bichloride of potassium 1 . . . 247 . . . 100·0

PLATINO-BICHLORIDE OF SODIUM. ($pla + 2c$) + ($so + c$).—Chloride of sodium occasions no precipitate with bichloride of platinum, but the mixed solutions yield on evaporation prismatic or tabular crystals, of a deep orange-colour, soluble in water and in alcohol, and which, when heated, lose 19·25 per cent. of water of crystallization, and leave the anhydrous double salt: the crystals, therefore, contain

Bichloride of platinum 1 . . . 171 . . . 60·0
Chloride of sodium 1 . . . 60 . . . 20·8
Water 6 . . . 54 . . . 19·2
Crystals of platino-bichloride of sodium 1 . . . 285 . . . 100·0

PLATINO-BICHLORIDE OF BARIUM.—When baryta-water is gradually added to a solution of bichloride of platinum, a precipitate falls composed of baryta and peroxide of platinum (*platinate of baryta*). The solution contains excess of baryta, which falls in the form of carbonate by exposure to air, and afterwards small crystals of the double salt are deposited. This salt may also be formed by mixing the two chlorides in atomic proportions: the crystals are orange-coloured, and in form and appearance resemble those of chromate of lead. They consist of

Bichloride of platinum 1 . . . 171 . . . 54·56
Chloride of barium 1 . . . 105 . . . 33·75
Water 4 . . . 36 . . . 11·69
Crystals of platino-bichloride of barium 1 . . . 312 . . . 100·00

PLATINO-CHLORIDES OF CALCIUM AND STRONTIUM have been described by Bonsdorff, as also those of *magnesium, manganese, iron, zinc, cadmium, copper, nickel, and cobalt*: the crystals of the last eight are isomorphous, and consist of 1 atom of the bichloride of platinum, 1 atom of the basic chloride, and 6 atoms of water.

PLATINO-CHLORIDE OF SILVER is thrown down as a yellow basic salt when solutions of bichloride of platinum and nitrate of silver are mixed; the residuary liquid remains colourless: boiling hydrochloric acid abstracts the chloride of platinum, and leaves the chloride of silver nearly without colour. (VAUQUELIN.)

PROTONITRATE OF PLATINUM is obtained by digesting the protoxide in dilute nitric acid: it is of a very deep brown colour, and is decomposed by evaporation, leaving peroxide of platinum.

PERNITRATE OF PLATINUM, formed by dissolving the peroxide in nitric acid, is of a dark-brown colour: when evaporated to dryness, water digested upon the residue leaves a subsalt. The addition of potassa throws down half the oxide, and afterwards a triple compound of nitric acid, oxide of platinum, and potassa.

PROTOSULPHURET OF PLATINUM. (*pla + s.*)—1. By heating platinum with sulphur in an exhausted glass tube. (E. DAVY.) 2. By heating ammonio-chloride of platinum with twice its weight of sulphur, to redness, in a covered crucible. (VAUQUELIN.) It is a gray or black powder; specific gravity 6·2; unaltered by air or water; scarcely attacked by the boiling acids; decomposed when ignited with chlorate of potassa. It consists of

				Vauquelin.	J. Davy.
Platinum	1	99	85·8	84·5	84
Sulphur	1	16	14·2	15·5	16
Protosulphuret of platinum	1	115	100·0	100·0	100

BISULPHURET OF PLATINUM. (*pla + 2 s.*)—When a solution of perchloride of platinum is mixed with sulphuret of ammonia or potassium a black powder falls, which when dried in vacuo over sulphuric acid, contains, according to Berzelius, no traces of water. When this precipitate is exposed upon paper to dry in the air, the sulphur absorbs oxygen, and becomes sulphuric acid, which chars the paper. When sulphuretted hydrogen is passed through solution of bichloride of platinum, the precipitate which falls consists of chloride and sulphuret of platinum. The bisulphuret consists of

				Vauquelin.	Berzelius.
Platinum	1	99	75·5	77	75·25
Sulphur	2	32	24·5	23	24·75
Bisulphuret of platinum	1	131	100·0	100	100·00

PROTOSULPHATE OF PLATINUM is obtained when a solution of protoxide of platinum in caustic potassa is saturated with sulphuric acid, the liquid poured off, and the precipitate dissolved in dilute sulphuric acid: the concentrated solution is opaque and black; diluted with water it becomes red, and appears gradually to pass into persulphate. Vauquelin

obtained this salt by digesting protochloride of platinum in sulphuric acid. The oxide is slowly precipitated from this sulphate by caustic alkali. (BERZELIUS.)

PERSULPHATE OF PLATINUM is obtained by acidifying the sulphur in the sulphurets, by means of nitric acid. It is of a very deep brown or almost black colour, and very soluble in water, alcohol, and ether; with soda, potassa, and ammonia, it forms double salts. It is a very delicate test of the presence of gelatine, with solutions of which it forms a brown precipitate.

FULMINATING PLATINUM.—E. Davy found that the precipitate from solution of sulphate of platinum by a slight excess of ammonia, when boiled in potassa, washed and dried, was a *fulminating platinum*; it explodes at about 420° , with a loud report, and appears to be a compound of oxide of platinum, ammonia, and water. (*Phil. Trans.*, 1817.) He has also described a compound of platinum, (*Phil. Trans.*, 1820, p. 108,) obtained by mixing equal volumes of strong aqueous solution of the sulphate and of alcohol. The colour of the sulphate slowly disappears, and in some days a black substance subsides, which is washed and dried. It is also formed by boiling the sulphate and alcohol together for a few minutes. This substance is permanent in the air and insoluble in water. It detonates feebly when heated, and is not affected by chlorine, nor by nitric, sulphuric, or phosphoric acids; but it is slowly soluble in hydrochloric acid. Put into liquid ammonia, it acquires fulminating properties; and plunged into ammoniacal gas it becomes red-hot: the same phenomenon is exhibited by exposing it to the vapour of alcohol, or by placing it upon a piece of paper moistened with that fluid: in these cases the platinum is reduced with the evolution of heat, and the ignition seems to depend upon the slow combustion of the vapour of the alcohol: some of these properties correspond with those of *platinum-black* (p. 990).

PHOSPHURET OF PLATINUM. (*pla + p*).—According to E. Davy, there are two phosphurets. The first, obtained by heating phosphorus with the metal: the second, by heating phosphorus with the ammoniochloride of platinum. Platinum crucibles are easily injured by the phosphorus evolved during the decomposition of phosphoric salts.

SELENIURET OF PLATINUM.—Selenium and finely-divided platinum combine with the evolution of heat into a gray powder, which is decomposed when heated in the air; selenium attacks platinum crucibles when evolved in them, and they may be cleansed by blowing a current of air into them when red hot.

CYANURET OF PLATINUM has not been obtained in a separate state, nor has the precipitate formed by ferrocyanuret of potassium in a strong solution of bichloride of platinum been satisfactorily examined. A double *cyanuret of platinum and potassium* is obtained according to L. Gmelin as follows: spongy platinum is mixed with its weight of ferrocyanuret of potassium and heated to incipient redness, but not higher: the platinum separates a part of the iron from the cyanogen, and when the mass is dissolved in water the platino-cyanuret may be separated by crystallization;

the crystals are yellow in one direction, but blue in the direction of their axes: they effloresce and become pale-red in the air, but still retain 12·4 per cent. of water, which requires a higher temperature for its separation. This salt is abundantly soluble in hot water, but the greater part crystallizes as the solution cools: the solution gives a scanty white precipitate, with solutions of the oxides of zinc, tin, and mercury; a pale-blue with the protosalts of iron, and a reddish-brown with the persalts of iron; a greenish blue with the salts of copper; and a white curdy precipitate which blackens by exposure to light, with nitrate of silver: it is not precipitated by nitrate of lead. This salt in crystals, consists, according to Gmelin, of

Platinum	1	99	45·2
Potassium	1	40	18·4
Cyanogen	2	52	23·9
Water	3	27	12·5
	1	218	100·0

SULPHOCYANURET OF PLATINUM forms, according to Grotthuss, a bulky flocculent precipitate of a yellow-colour: it is soluble in acids and in solutions of chloride of potassium and sodium, and of sal-ammoniac: alcohol throws it down again from these solutions.

ALLOYS OF PLATINUM.—With *potassium* and *sodium* it forms compounds which decompose water. (DAVY.) Its alloy with *manganese* is unknown. *Iron* and platinum in equal parts form a crystalline alloy which takes a fine polish. According to Dr. Lewis, the alloy of cast iron and platinum is hard, tough, and somewhat ductile, the density greatly exceeding the mean: it is brittle when hot. Stodart and Faraday found the toughness and smoothness of steel improved by one hundredth of platinum. (*Phil. Trans.*, 1822.) Wires of steel and platinum, when welded and polished, exhibit a curious and beautiful surface, especially when the steel parts are slightly acted upon by dilute acid. This welding property of platinum may be usefully applied in the arts; wires may be joined so as to form rings and chains; and with a view to economy, platinum may be joined to iron or steel for many uses in the laboratory of the chemist. Platinum dissolves in fused *zinc*; the alloy is bluish-white, brittle, and hard: one twentieth of platinum destroys the malleability of zinc, and one fourth of zinc renders platinum brittle. (LEWIS.) *Tin* and platinum combine in all proportions, forming alloys more or less brittle and fusible. When tin-foil and platinum are wrapped together and heated by the blowpipe, they combine with incandescence. (Fox, *Ann. Phil.*, xiii. 467.) The alloy of *cadmium* and platinum is white, granular, brittle, and easily fusible: heated till the excess of cadmium is expelled, it contains 100 platinum+117 cadmium. (THOMSON.) The alloy of *cobalt* and platinum is comparatively fusible. With its weight of *nickel* platinum forms a pale-yellow alloy, susceptible of a high polish, and obedient to the magnet. *Copper* and platinum form alloys, the ductility and colour of which, vary with the proportions. Platinum easily destroys the colour of copper: this compound has been recommended for the mirrors of reflecting telescopes: an alloy of 7 platinum, 16 copper, 1 zinc, resembles gold in colour. (COOPER, *Quart. Journ.*, iii. 119.) *Lead* and

platinum form brittle alloys, not entirely decomposed by cupellation. (DUMAS.) *Antimony* forms a gray compound with platinum, partly decomposed by heat; and entirely, by roasting: these metals enter into ignition when they combine, in the same manner as tin and zinc. (FOX.) *Bismuth* and platinum form brittle alloys not entirely decomposed by cupellation. (LEWIS.) *Arsenic* and platinum form a dark-gray, brittle alloy. When particles of arsenic are placed upon red-hot platinum-leaf, they immediately fuse a hole in it. When 2 parts of platinum, 2 of arsenious acid, and 1 of potassa, are fused together, a compound of 89 platinum, and 10 of arsenic (1 atom of each), is obtained: its density is 16.4; it is fusible at a red heat, but the whole of its arsenic cannot be expelled by heat. Equal parts of *molybdenum* and platinum melted into a hard, brittle mass: when the proportion of platinum was increased, the fusion was not complete. (HIELM.) *Mercury* amalgamates difficultly with platinum: a compound of 63 of mercury, and 37 of platinum, is a soft solid: spongy platinum forms the readiest combination: this amalgam adheres well to the surface of glass. *Silver* and platinum form fusible and ductile alloys; when the silver predominates they are soluble in nitric acid; by boiling sulphuric acid, the silver only is dissolved. When the alloy is kept in fusion, its components have a tendency to separate. *Gold* and platinum require a strong heat for combination, and the colour of the gold is greatly deteriorated even by one-twenty-second of platinum: an alloy of 4 of platinum, and 1 of gold, nearly resembles platinum in colour; the gold colour does not predominate till it forms eight-ninths of the alloy. (HATCHETT. KLAPROTH.)

The perfection with which vessels of platinum resist the action of heat and air, of most of the acids, and of sulphur and mercury, render them peculiarly valuable in many of their applications; but its high value is against its very general adoption, for, although much cheaper than gold, it is worth between four and five times its weight of silver. Berzelius observes (LEHRBUCH), that in the employment of platinum vessels, the following precautions must be attended to: 1. They must not be subjected to the action of compounds which evolve chlorine. 2. Nitre, and the alkalis, must not be fused in them. 3. No metallic reductions must be performed in them; nor compounds of phosphorus decomposed so as to evolve that substance. 4. When metallic oxides are heated in a platinum crucible, the heat must not be raised beyond redness, provided the oxide is easily decomposed: hence the caution requisite with the oxides of lead, bismuth, copper, cobalt, nickel, and antimony, which, though they may not effect the fusion of the crucible, spoil it by their action upon its interior surface, which is rendered rough and porous. 5. That the immediate contact of the fuel (charcoal should always be used) with the crucible should be avoided as much as possible, especially at very high temperatures; for it is thus, in the process of time, rendered brittle and unsound. Small holes and fissures may be filled up and soldered with pure gold, but in that case the vessel must not be exposed to a white heat, because then the gold and platinum combine. It would appear from Mr. Daniell's experiments (*On a new register pyrometer*, *Phil. Trans.*, 1831, p. 315,) that one cause of the brittleness which platinum acquires when repeatedly heated in the usual fuel, depends upon

the absorption of silicium, to the amount of about 3 per cent. A high temperature appears necessary to effect this combination, which is somewhat analogous to the absorption of carbon by iron in the process of making steel by cementation.

CHARACTERS OF THE SALTS OF PLATINUM.—The difficult solubility of the ammonio and potasso-chlorides of platinum, and the solubility of the corresponding soda-compounds, are very characteristic of this metal. Phosphate of soda produces no precipitate in chloride of platinum; the ferrocyanurets of potassium throw down the platino-chloride of potassium: cyanuret of mercury occasions no precipitate: iodide of potassium communicates a reddish-brown colour to solutions of the chlorides of platinum, and gradually produces a brown precipitate; and if the mixture be heated in a matrass, the glass acquires a coating of metallic platinum. All the metals which reduce the chloride of gold, with the exception of palladium, act similarly upon chloride of platinum, but its complete separation in the metallic state is slow: iron, zinc, cadmium, and copper, are its most effective precipitants; they separate it as a black powder, which sometimes adheres in films to the glass.

§ XXXIV. PALLADIUM.

PALLADIUM was discovered by Wollaston in 1803: it is always associated with the other metals mentioned in the last section as constituting the ore of platinum: it has also been found by M. Zinken in the gold and lead ores of the duchy of Anhalt Bernburg (*Ann. de Ch. et Ph.*, xliv. 201), and is common in Brazilian gold.

Palladium is separated from the ore of platinum by the following process. (WOLLASTON, *Phil. Trans.*, 1805.) Digest the ore in nitrohydrochloric acid, neutralize the redundant acid by soda, throw down the platinum by sal-ammoniac, and filter: to the filtered liquor add a solution of cyanuret of mercury: a yellow flocculent precipitate of cyanuret of palladium is soon deposited, which yields palladium on exposure to heat.

To obtain malleable palladium, Dr. Wollaston gives the following more explicit directions. (*Phil. Trans.*, 1819.) "The residuum obtained from burning the cyanuret of palladium is to be combined with sulphur, and each cake of the sulphuret, after being fused, is to be finally purified by cupellation, in an open crucible, with borax and a little nitre. The sulphuret is then to be roasted, at a low red-heat, on a flat brick, and pressed, when reduced to a pasty consistence, into a square or oblong and perfectly-flat cake. It is again to be roasted very patiently, at a low red-heat, until it becomes spongy on the surface. During this process sulphur flies off in the state of sulphurous acid, especially at those moments when the heat is allowed occasionally to subside. The ingot is then to be cooled; and when quite cold, is to be tapped with a light hammer, in order to condense and beat down the spongy excrescences on its surface. The alternate roastings and tappings (or gentle hammerings) require the utmost patience and perseverance, before the cake can be brought to bear hard blows; but it may, by these means, at length be made so flat and

square, as to bear being passed through the flatting-mill, and so laminated to any required degree of thinness. Thus prepared, it is always brittle while hot, possibly from its still containing a small remnant of sulphur. I have also fused some palladium *per se*, without using sulphur; but I have always found it, when treated in this way, so hard and difficult to manage, that I greatly prefer the former process."

Palladium is of a dull-white colour, malleable and ductile. Its specific gravity is about 11·3, or 11·86 when laminated. Its specific heat is 0·05927. (REGNAULT.) It is hard. It fuses at a temperature above that required for the fusion of gold, and when intensely heated by the oxy-hydrogen blowpipe, it is dissipated in sparks. When heated over the flame of a spirit-lamp, it acquires various shades of blue upon its surface, in consequence of superficial oxidation. It is acted on by the greater number of the acids when aided by heat, and also by potassa and nitre: it is blackened when an alcoholic solution of iodine is evaporated from its surface, which is not the case with platinum: it has a strong affinity for cyanogen. The equivalent of palladium appears to be somewhere between 52 and 57. I have adopted 54. (53·3 TURNER. 56 GMELIN.)

Dr. Wollaston has ascertained the existence of *native palladium* in the ore of platinum. It is in small fibrous grains.

PROTOXIDE OF PALLADIUM. (*pal*+*o*).—By carefully heating the nitrate of palladium to dull redness, a black oxide is obtained, which dissolves in hydrochloric acid without evolving chlorine. When nitrate of palladium is precipitated by an alkali, the red or dark-orange coloured powder which falls, is an *hydrated oxide*. This oxide consists of

				Berzelius.			
Palladium	1	54	87	87	56		
Oxygen	1	8	13	12	44		
Protoxide of palladium				1	62	100	100·00

BINOXIDE OF PALLADIUM. (*pal*+*2o*).—To prepare this oxide Berzelius recommends that a solution of potassa, or its carbonate, in excess, should be poured by little and little on the solid bichloride of palladium and potassium, and the materials well intermixed; water is not first added, because it decomposes the double chloride, and the alkali is not added all at once, because the oxide would then be dissolved at first, and afterwards separate as a gelatinous hydrate, which could not be purified by washing. When prepared according to the foregoing directions, the binoxide is obtained as a hydrate, of a deep yellowish-brown colour, which retains a little potassa in combination, but on heating the solution to 212° the alkali is dissolved, and the anhydrous black oxide left. (TURNER'S *Elements*.)

SULPHATE OF PALLADIUM is formed by digesting the metal in sulphuric acid, or by decomposing the nitrate by that acid: it is a soluble red salt.

PROTOCHLORIDE OF PALLADIUM (*pal*+*c*) is obtained by digesting palladium in hydrochloric acid with a little nitric acid, and evaporating to dryness: it forms a brown powder, which is black when rendered

anhydrous. It forms double salts with most of the other chlorides. It consists of

Palladium	1	54	60
Chlorine	1	36	40
<hr/>			
Protochloride of palladium	1	90	100

AMMONIO-PROTOCHLORIDE OF PALLADIUM is a soluble salt which is convertible into perchloride of palladium, by boiling with nitrohydrochloric acid. By adding excess of ammonia to this salt, another ammonio-chloride is formed, which is an insoluble yellow powder.

PALLADIO-PROTOCHLORIDE OF POTASSIUM is formed by dissolving (*pal*+*c*) with (*po*+*c*). It crystallizes in four-sided prisms, soluble in water and precipitated from this solution by alcohol in the form of brilliant yellow scales. The corresponding *sodium salt* is soluble in alcohol, and deliquescent.

PERCHLORIDE OF PALLADIUM. BICHLORIDE OF PALLADIUM. (*pal*+ $2c$).—Obtained by dissolving the protochloride in nitrohydrochloric acid, and applying a gentle heat: the solution is almost black, and gives a red precipitate with chloride of potassium: when the solution is boiled, chlorine is evolved, and protochloride formed. It consists of

Palladium	1	54	42·8
Chlorine	2	72	57·2
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Bichloride of palladium	1	126	100·0

PALLADIO-BICHLORIDE OF POTASSIUM. (*pal*+ $2c$)+(*po*+*c*).—When the palladio-protochloride of potassium is digested in nitrohydrochloric acid and evaporated to dryness, the above compound is obtained in the form of a red crystalline powder: it is very sparingly soluble in cold water, and hot water partially decomposes it with the formation of hydrochloric acid and binoxide of palladium: heated till it fuses, it evolves chlorine, and becomes the protosalt. The corresponding *ammoniacal salt* is also of a cinnabar-red colour.

NITRATE OF PALLADIUM.—Palladium, especially when aided by heat, dissolves in nitric acid, forming a red solution, which leaves a red subnitrate on evaporation.

SULPHURET OF PALLADIUM. (*pal*+*s*).—This compound is readily formed by fusing sulphur with palladium; it is white, hard, and fusible, and when long exposed to heat and air loses the whole of its sulphur. It is thrown down in the form of a black powder, by the action of sulphuretted hydrogen upon the salts of palladium. It consists of

				Berzelius.	Vauquelin.
Palladium	1	54	77·1	78	80·6
Sulphur	1	16	22·9	22	19·4
<hr/>					
Sulphuret of palladium	1	70	100·0	100	100·0

PHOSPHURET OF PALLADIUM is an easily-fusible compound.

SELENIURET OF PALLADIUM.—Selenium and palladium combine, with the evolution of heat; the compound is gray and coherent, but does not fuse: before the blowpipe it gives off selenium, and at a very high temperature melts into a gray metallic button, which is brittle and crystalline, and still retains selenium.

CARBURET OF PALLADIUM.—Palladium acquires extreme brittleness when long fused in contact with charcoal. When a plate of palladium is held in the flame of alcohol, it becomes covered with carbon, and carbonaceous excrescences gradually form upon it, which, when burned, leave palladium, and the surface of the metal becomes corroded, and its whole substance brittle. When spongy palladium, in the state in which it is obtained by the ignition of its ammonio-chloride, is heated to redness, and placed upon the wick of a spirit-lamp, it glows and becomes enveloped in an accumulation of a compound of carbon and palladium. This property of precipitating charcoal from flame, and combining with it, is peculiar to palladium. Platinum and iron show indications of it. (Wöhler, *Poggend.*, iii. 71.)

CYANURET OF PALLADIUM.—This compound is formed when a solution of cyanuret of mercury is added to a neutral solution of palladium: it falls in olive-coloured or dingy-yellow flakes: this furnishes a ready method of separating palladium from other metals which are incapable of decomposing the cyanuret of mercury. The cyanuret of palladium, when sufficiently heated, leaves the metal: it dissolves in cyanuret of potassium, and, on evaporation, prismatic crystals of *palladio-cyanuret of potassium* are obtained. There is also a corresponding *ammoniacal salt*. When nitrate of palladium is decomposed by cyanuret of mercury, the precipitate detonates by heat.

ALLOYS OF PALLADIUM.—These have not been minutely examined. Like platinum, it destroys the colour of gold; 1 part, fused with 6 of gold, forming a white alloy. This compound, from its hardness and durability, was employed, at the suggestion of Dr. Wollaston, for the graduated part of the mural circle, constructed by Troughton for the Royal Observatory at Greenwich. It readily amalgamates with mercury. Palladium exists in large quantities in some part of South America, for bars of it, weighing several pounds, have been imported from that country, and nearly pure.

CHARACTERS OF THE SALTS OF PALLADIUM.—The fixed alkalis throw down red or orange-coloured precipitates from the solutions of palladium, sparingly soluble in excess of the alkali. Ferrocyanuret of potassium gives an olive-green precipitate; and sulphuretted hydrogen one of a dark-brown colour. Protochloride of tin occasions a brown precipitate in the neutralized solutions of palladium; when dilute, the mixture becomes green. Protosulphate of iron throws down metallic palladium. Many of the other metals precipitate palladium in the metallic state. Cyanuret of mercury forms a precipitate in all the salts of palladium when the acid is not in excess.

§ XXXV. RHODIUM.

THIS metal, discovered in 1803, by Wollaston, may be obtained as follows:—Digest the *ore* of platinum in nitrohydrochloric acid, filter the saturated solution, and pour it into a solution of sal-ammoniac, by which the greater proportion of the platinum is precipitated; filter, and separate the palladium by cyanuret of mercury; filter again, and immerse a plate of zinc into the clear solution, which will become coated with a black powder. Separate this, and digest it in dilute nitric acid, by which a little copper and lead are taken up. Then wash, and digest in dilute nitrohydrochloric acid, to which add some common salt; evaporate to dryness, and wash the dry mass repeatedly with alcohol. A deep-red substance remains, which, when dissolved in water, furnishes a black precipitate upon the immersion of a plate of zinc. This, strongly heated with borax, assumes a white metallic lustre, and is rhodium.

Rhodium is a white metal very difficult of fusion: its specific gravity is about 11; it is extremely hard. When pure, the acids do not dissolve it, but they act upon and dissolve several of its alloys, a circumstance which explains its presence in the nitrohydrochloric solution of platinum. When an alloy of lead and rhodium is digested in nitrohydrochloric acid, it is also readily dissolved, and by evaporation a red compound is obtained, from which chloride of rhodium may be separated by water. The *red-colour* of this compound suggested the name which has been applied to the metal (from $\rho\acute{o}\delta\delta\omicron\nu$, a rose). Berzelius has shown that metallic rhodium may be oxidized by ignition either with nitre or with bisulphate of potassa, and that when heated with the latter, a double sulphate of peroxide of rhodium and potassa is produced, which yields a yellow solution with hot water: in this way rhodium may be separated from platinum, iridium, and osmium. There is great discrepancy in the equivalent of rhodium given by different chemists; according to the latest experiments of Berzelius, the number 52 has been adopted. (52.2 TURNER. 54 THOMSON. 120 GMELIN. 45 deduced from earlier experiments.)

PEROXIDE OF RHODIUM. SESQUIOXIDE OF RHODIUM.—When a mixture of finely-divided rhodium, potassa, and a little nitre, is heated to redness in a silver crucible, and the product washed with water, and then digested in hydrochloric acid, a hydrated peroxide of rhodium, insoluble in the acid, remains. When heated it becomes black, and probably is then the *protoxide*. This oxide is stated to consist of

Rhodium	1	52	81
Oxygen	$1\frac{1}{2}$	12	19
Sesquioxide of Rhodium	1		64		100

PERCHLORIDE OR SESQUICHLORIDE OF RHODIUM was obtained by adding silicated fluoric acid to a solution of rhodio-chloride of potassium, as long as the silico-fluoride of potassium was generated, after which the filtered liquid was evaporated to dryness, and [the residue] redissolved in water. This perchloride when dry has a dark-brown

colour, is uncrystalline, and decomposed by a full red-heat into chlorine and metallic rhodium. It deliquesces in the air into a brown liquid, and its aqueous solution has a fine red colour. (*Ann. de Ch. et Ph.*, XL. 51.)

This perchloride is represented as consisting of

Rhodium	1	52	49
Chlorine	$1\frac{1}{2}$	54	51
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Sesquichloride of rhodium	1	106	100

In combination with the chlorides of potassium and sodium, this perchloride forms double salts. (*rhodio-chlorides*.) They are composed of 1 atom of the perchloride and 1 of the basic chloride.

NITRATE OF RHODIUM is formed by dissolving the oxide in nitric acid; it is deliquescent, uncrystallizable, and of a deep red colour. The double *nitrate of rhodium and soda* forms dark-red crystals, soluble in water, but insoluble in alcohol.

SULPHURET OF RHODIUM is obtained by heating the metal in a state of fine division with sulphur; or by heating the ammonio-chloride of rhodium with sulphur: it is also precipitated by heating the solution of the latter salt with one of an alkaline hydrosulphuret.

SULPHATE OF RHODIUM is a soluble uncrystallizable salt, obtained by the action of nitric acid on precipitated sulphuret of rhodium; it forms two double sulphates with potassa; one is obtained by igniting rhodium with bisulphate of potassa; it yields a yellow solution with hot water; the other is formed by the action of sulphurous acid on the rhodio-chloride of potassium; it is a pale yellow powder.

ALLOYS OF RHODIUM.—Rhodium forms malleable *alloys* with the malleable metals, several of which have been examined by Dr. Wollaston. (*Phil. Trans.*, 1804.) It has not been combined with mercury.

With *steel*, rhodium forms an alloy, which probably would be very useful in the arts, were it not for the scarcity of the latter metal. 1 to 2 per cent. of rhodium gives steel great hardness, and yet there is sufficient tenacity to prevent cracking either in forging or hammering. (*Quarterly Journal*, ix. 328.) The extreme hardness and durability of rhodium induced Dr. Wollaston to suggest it for the nibs of metallic pens, a purpose to which it has been successfully applied.

CHARACTERS OF THE SALTS OF RHODIUM.—These have as yet been but imperfectly examined. Those containing the peroxide are mostly of a red or orange colour; they are precipitated by cyanuret of mercury, by ferrocyanuret of potassium, and by sal-ammoniac. The action of the pure alkalis upon them is very indefinite. According to Pfaff (*Handbuch der Analyt. Chemie*), the salts of the peroxide of rhodium yield a yellow flocculent precipitate insoluble in excess of the precipitant, with the caustic alkalis: they are not precipitated by carbonated alkalis, nor by solution of sal-ammoniac, if there be excess of acid present; but the perchloride of rhodium yields a difficultly-soluble dingy-yellow precipitate, with excess of ammonia; hydrochloric acid redissolves it, and forms a red solution. Zinc and iron throw down metallic rhodium.

§ XXXVI. OSMIUM.

OSMIUM and Iridium are contained in the black powder which remains after the action of nitrohydrochloric acid upon the ore of platinum. This residue, when fused with potassa and washed, furnishes a yellow alkaline solution of oxide of osmium. Saturate the alkali with sulphuric acid, pour the mixture into a retort, and distil. A colourless solution of the *oxide of osmium* passes into the receiver, from which almost all the other metals throw down metallic osmium. (TENNANT, *Phil. Trans.*, 1804; WOLLASTON, *Ibid.*, 1829.)

To obtain the oxide of osmium in a pure, solid, and crystallized state, grind together, and introduce, when ground, into a cold crucible, three parts by weight of the insoluble powder, and one part of nitre. The crucible is to be heated to a good red in an open fire, until the ingredients are reduced to a pasty state, when osmic fumes will be found to arise from it. The soluble parts of the mixture are then to be dissolved in the smallest quantity of water necessary for the purpose, and the liquor thus obtained is to be mixed in a retort, with so much sulphuric acid, diluted with its weight of water, as is equivalent to the potassa contained in the nitre employed: but no inconvenience will result from using an excess of sulphuric acid. By distilling rapidly into a clean receiver, for so long a time as the osmic fumes continue to come over, the oxide will be collected in the form of a white crust on the sides of the receiver, and there melting, it will run down in drops beneath the watery solution forming a fluid flattened globule at the bottom. When the receiver has become quite cold, the oxide will become solid and crystalline. One such operation has yielded 30 grains of the crystallized oxide, besides a strong aqueous solution of it. This may be agitated with mercury, and the product washed with hydrochloric acid to remove the oxide of mercury which is formed. The osmium remains in the form of a black powder, which acquires a metallic lustre by friction. In its densest state, its specific gravity, according to Berzelius, is 10. (*Ann. de Ch. et Ph.*, xl. and xlii.) When heated in the air it burns into an oxide, and in its pulverulent state it is attacked by nitric acid; but after exposure to a red-heat in close vessels, it becomes much less oxidable. Osmium is extremely poisonous, and has an extraordinary influence upon the brain and nervous system; so that persons have been rendered delirious by inhaling osmic fumes. The equivalent of osmium appears, on the authority of Berzelius, to be about 100, (99.7 TURNER,) and he conceives it susceptible of five degrees of oxidizement.

PROTOXIDE OF OSMIUM ($Os + O$) is obtained by the action of pure alkalis on the protochloride of osmium, or upon the osmio-chloride of potassium: it gradually falls in the form of a nearly black *hydrate*, obstinately retaining a portion of alkali; it dissolves slowly in the acids forming deep-green or greenish-brown solutions. When heated in a close vessel it gives off water, but does not sublime. It detonates when heated with combustibles. Its equivalent is 108.

SESQUIOXIDE OF OSMIUM ($Os + 1\frac{1}{2}O$) has not been obtained in an insu-

lated state, but is produced in combination with ammonia, when the bin-oxide is heated with excess of ammonia, nitrogen being at the same time evolved.

BINOXIDE OF OSMIUM. ($Os + 2O$).—When a saturated solution of bichloride of osmium, or of the osmio-bichloride of potassium, is heated with carbonate of soda, the binoxide gradually falls; it retains a little alkali, which may be removed by dilute hydrochloric acid; if it then be washed and dried at 212° , it only retains water, which it gives off when heated, and remains anhydrous. In this state it appears insoluble in the acids. Its equivalent is 116.

TEROXIDE OF OSMIUM ($Os + 3O$) is assumed to exist in certain salts of this metal, but has not been isolated.

PEROXIDE OF OSMIUM. OSMIC ACID. ($Os + 4O$) or Os' .—This is the volatile oxide above adverted to, and is obtained by the combustion of the metal in oxygen, or by the action of boiling nitric acid, or by the fusion of osmium with nitre or with potassa. When osmium is heated, and a current of oxygen passed over it, white or yellowish crystals of the anhydrous peroxide are formed: these dissolve slowly in water, and readily in alcohol and ether; the solutions gradually deposit metallic osmium. Other combustibles deoxidize it; by sulphurous acid its solution is rendered yellow, orange, brown, green, and lastly blue, colours corresponding to the different degrees of oxidizement. It stains the skin. It may be volatilized in hydrogen gas, but when its vapour and hydrogen are passed through a red-hot tube, it is reduced. It is reduced by sulphuretted hydrogen, and sulphuret of osmium is formed. The odour of the vapour of this oxide is very peculiar; it has been by some compared to that of chlorine; it is acid, and poisonous; when much diluted, it a little resembles the smell of new wheaten bread; this is the origin of the term *osmium*, from $\delta\sigma\mu\eta$, *odor*. It has no acid reaction, but as it combines with alkalis, and forms compounds which are permanent at high temperatures, it has sometimes been termed *osmic acid*. When infusion of galls is dropped into its aqueous solution, a very characteristic blue colour is produced, which Berzelius ascribes to a mixture of the peroxide and sesquioxide. The equivalent of this oxide is $100 + 32 = 132$.

CHLORIDES OF OSMIUM.—Berzelius has described four chlorides of this metal, corresponding in composition to the oxides. When chlorine is transmitted over heated osmium, a beautiful dark-green sublimate of *protochloride of osmium* is the result. This is succeeded by a red sublimate, which is the *bichloride*. The *sesquichloride* and *perchloride* have not been obtained in a separate state, but Berzelius infers their existence in combination with sal-ammoniac, in certain *osmio-chlorides* of that salt: he has also examined the double salts, produced by the union of the protochloride and perchloride of osmium with the chloride of potassium.

SULPHURETS OF OSMIUM.—Sulphur and osmium apparently combine, in several proportions, for sulphuretted hydrogen precipitates it from all its solutions.

The remaining compounds of this remarkable metal have not been suffi-

ciently examined, to enable us to give satisfactory details respecting them. A few of its *alloys* have been noticed by Mr. Tennant, and the characters of its salts will be sufficiently obvious from the preceding statements.

§ XXXVII. IRIDIUM.

THIS metal was discovered by Tennant in 1803, and about the same time by Descotils: the various colours exhibited by the hydrochloric solution of its oxide suggested its name (from *Iris*, the rainbow). The black powder which remains after native platinum has been digested in nitrohydrochloric acid, consists chiefly of iridium and osmium; titanium and chromate of iron also occur in it. To obtain iridium, this powder is fused in a silver crucible, with twice its weight of hydrate of potassa, for the space of an hour or more; the residue is washed, by which, as already stated, the oxide of osmium is removed, and the remaining insoluble portion is *iridium*, which has been oxidized by the process of fusion. This oxide is soluble in hydrochloric acid, and the solution is blue, if free from iron, which communicates more or less of a green tint: when heated with the addition of a little nitric acid, it becomes red, probably in consequence of the peroxidizement of the iridium. When the hydrochloric solution of iridium is evaporated, it furnishes brown crystals, which are decomposed by a red-heat, and leave finely-divided metallic iridium. They form a reddish-brown solution with water, which, if concentrated and mixed with a saturated solution of sal-ammoniac, afford a dark-brown precipitate of the *ammonio-chloride of iridium*. The solution of the chloride is decomposed by all the metals except gold and platinum, and metallic iridium precipitated.

Iridium, obtained by immersing a plate of zinc into a solution of the chloride, or by violently heating that salt, is of a whitish colour, and, according to Mr. Children, who succeeded in fusing it by means of his large Voltaic apparatus, its specific gravity is above 18. The approximate specific heat of iridium is, according to Regnault, $= 0.03683$. Its most marked character is extremely difficult solubility in the acids: indeed, when pure, it is probably insoluble, although, when alloyed with platinum, a little is taken up by nitrohydrochloric acid. Its equivalent, deduced from the experiments of Berzelius, is 96. The following details respecting the combinations of iridium are abridged from Berzelius, and from Dumas. (*Chim. app. aux Arts.*)

OXIDES OF IRIDIUM.—According to Berzelius there are four oxides of iridium, separable from the corresponding *chlorides* by the action of alkalis.

PROTOXIDE OF IRIDIUM ($ir + o$) is obtained by decomposing the protochloride by a solution of caustic potassa; the product is to be washed with dilute acid, and afterwards with water and dried; it is a heavy black powder which loses oxygen at a red heat; it is not soluble in the acids, but with potassa yields a blue or purple solution. The hydrate of this oxide is thrown down in the form of a greenish-gray powder, when the iridiochloride of potassium ($ir + c$) + ($po + c$) is decomposed by carbonate of potassa. This oxide consists of

Iridium	1	96	92.3
Oxygen	1	8	7.7
Protoxide of iridium	1	104	100.0

DEUTOXIDE OR SESQUIOXIDE OF IRIIDIUM ($ir + 1\frac{1}{2}o$) is formed when iridium is calcined with nitre or caustic potassa; or by exposing a mixture of the iridiobichloride of potassium ($ir + 2cl$) + ($po + c$) with twice its weight of carbonate of potassa to a dull red heat; the residue when washed leaves this oxide in the form of a black powder; it requires a very high red heat for its decomposition; hydrogen gas decomposes it at common temperatures, in consequence probably of an action similar to that of spongy platinum. The hydrate of this sesquioxide is obtained in the form of a bulky dark reddish-brown precipitate, when a solution of the sesquichloride, or one of its double salts, is decomposed by an alkali; if ammonia be used, the precipitate deflagrates when heated. The saturated alkaline solutions of this sesquioxide are decomposed when diluted with water; its hydrate combines with acids, but when anhydrous it is insoluble in them. The components of this oxide are

Iridium	1	96	88.9
Oxygen	$1\frac{1}{2}$	12	11.1
Sesquioxide of iridium	1	108	100.0

BINOXIDE OF IRIIDIUM ($ir + 2o$) has not been isolated, but it exists in a class of salts, and appears to be soluble in the alkalis and their carbonates.

PEROXIDE OF IRIIDIUM ($ir + 3o$) is obtained by gently heating a mixed solution of perchloride of iridium and carbonate of potassa; it falls in the form of a yellow or greenish precipitate, not however free from alkali; if dried and heated, it is decomposed with decrepitation. When the double iridioperchlorides are decomposed by excess of ammonia, a blue oxide is obtained which yields blue solutions with the acids, and is regarded by Berzelius as a compound of the protoxide and sesquioxide. The peroxide consists of

Iridium	1	96	80
Oxygen	3	24	20
Peroxide of iridium	1	120	100

PROTOCHLORIDE OF IRIIDIUM ($ir + c$) is formed by the action of chlorine on iridium heated to incipient redness; it is a dark-olive powder; it is decomposed at a high heat, giving off chlorine and sesquichloride, and leaving iridium; it is insoluble in water; very slightly soluble in boiling hydrochloric acid, and scarcely affected by nitrohydrochloric acid; it is resolved by excess of potassa into chloride of potassium and protoxide of iridium; it forms double iridio-protochlorides. Its components are

Iridium	1	96	72.8
Chlorine	1	36	27.2
Protochloride of iridium	1	132	100.0

SESQUICHLORIDE OF IRIIDIUM. ($ir + 1\frac{1}{2}c$).—When iridium is calcined with potassa and nitre, and the resulting product supersaturated by nitric

acid, an oxide is obtained, which when washed, and dissolved in hydrochloric acid, yields chloride and sesquichloride of iridium; the latter forms a brown solution, which, evaporated to dryness and digested in alcohol, gives a solution of sesquichloride, and a residue of the double iridiochloride of potassium. The sesquichloride is obtained on evaporating the alcoholic solution, in the form of a deliquescent uncrystallizable compound of a black hue; it tinges water deep brown; it is always hydrated, and, when heated, gives off hydrochloric acid, and forms an oxichloride which is decomposed at a higher heat. This chloride forms double salts with the alkaline chlorides; their solutions are deep brown, and, when boiled with excess of alkaline chloride, are decomposed, the sesquichloride of iridium becoming protochloride and bichloride, and forming two double salts, of which those of the protochloride are dissolved, and those of the bichloride deposited. The sesquichloride consists of

Iridium	1	96	64
Chlorine	$1\frac{1}{2}$	54	36
Sesquichloride of iridium	1	150	100

BICHLORIDE OF IRIIDIUM ($ir + 2c$) is obtained by calcining iridium with nitre and potassa, washing the resulting oxide, dissolving it in nitrohydrochloric acid and evaporating to dryness; the bichloride remains nearly pure; at a high heat, it gives out water and hydrochloric acid, and produces oxide of iridium; its aqueous solution is deep red; it is soluble in alcohol, but this solution decomposes spontaneously into hydrochloric acid, sesquichloride, and iridium. Bichloride of iridium consists of

Iridium	1	96	57.2
Chlorine	2	72	42.8
Bichloride of iridium	1	168	100.0

IRIDIO-BICHLORIDES.—The bichloride of iridium produces characteristic double salts. When an intimate mixture of metallic iridium and chloride of potassium is heated, and subjected to the action of a current of chlorine, the *iridio-bichloride of potassium* is formed; the resulting product should be washed in water acidulated by nitrohydrochloric acid; the undissolved iridium separated by decomposition, and the solution evaporated to dryness; the excess of chloride of potassium may then be removed by water, for the double chloride is insoluble in the solution of that salt. Thus purified, the double salt may be again dissolved in the acidulated water, and obtained, by due evaporation, in anhydrous octoëdral crystals. This salt is black in mass, but red in powder; it is insoluble in alcohol, which throws down a brown or deep red precipitate from its solutions; it is not fusible, nor decomposed at a dull red heat; a higher temperature converts it into sesquichloride, and an intense heat into chlorine and metallic iridium, which remains mixed with chloride of potassium. *Iridio-bichloride of sodium* is prepared as the preceding, and has the same general properties, but it includes water of crystallization, and forms tabular, or quadrangular prismatic crystals with diëdral summits. When a solution of bichloride of *iridium* is mixed with one of *sal-ammoniac*, a double salt is obtained, little soluble in water, and insoluble in alcohol, and which, when heated, leaves pure iridium; it is of so deep-red a colour as to

appear almost black, and the slightest traces of it give a red tinge to the ammonio-chloride of platinum; 1 part dissolved in 20 of water form a very deep orange-coloured solution; indeed, according to Vauquelin, its colouring power is so great, that 1 part of it gives a decided tint to 40,000 of water. Ammonia decolours this solution without producing a precipitate; protosulphate of iron, sulphuretted hydrogen, and zinc, iron, and tin, produce the same effect, and chlorine restores the colour. This double salt consists of

Bichloride of iridium	1	168	75.6
Hydrochlorate of ammonia . .	1	54	24.4
Ammonio-bichloride of iridium	1	222	100.0

SULPHURETS OF IRIIDIUM.—When the respective chlorides of iridium are decomposed by sulphuretted hydrogen, a series of sulphurets corresponding with the chlorides appear to be formed; they are of a deep brown, and resemble the sulphurets of platinum, rhodium, and palladium: they are soluble in potassa and in carbonate of potassa, and in alkaline sulphurets. When equal parts of sulphur and of the preceding ammonio-bichloride are heated together, a bisulphuret is obtained, composed of

Iridium	1	96	75
Sulphur	2	32	25
Bisulphuret of iridium	1	128	100

SULPHATES OF IRIIDIUM.—When the sulphurets prepared by precipitation are digested, whilst moist, in cold nitric acid, they are converted into sulphates of iridium, which are dark green, brown, or orange, according as they contain the protoxide, sesquioxide, or binoxide.

PHOSPHURET OF IRIIDIUM is obtained by heating the metal in the vapour of phosphorus; a compound resembling iridium in appearance is formed, which burns, when heated red-hot, in the air, and is converted into iridium, and phosphate of oxide of iridium.

CARBURET OF IRIIDIUM.—When iridium is immersed in the flame of alcohol, black excrescences of carburet form upon it, which, burned in the air, leave pure iridium, so that, as soon as it is formed by the above process, it must be immediately dropped into water on withdrawing it from the flame; its composition appears to be (*ir* + 4*car*.)

ALLOYS OF IRIIDIUM.—These require a very high heat for their formation; the ductile metals may be combined with a considerable proportion of iridium without loss of ductility. The greater number of these alloys, when digested in nitric acid, leave a pulverulent residue of iridium; nitrohydrochloric acid dissolves them when the proportion of iridium is not very considerable.

The *native alloy of iridium and osmium* forms small crystals of much lustre, harder than steel, and as refractory as iridium; they fuse, however, as well as iridium, in the arc of flame between the charcoal points of a powerful voltaic battery. (DANIELL.) The density of these grains is 18.64.

SALTS OF IRIIDIUM.—These salts have not been minutely examined;

those obtained by dissolving the hydrated protoxide are generally green and uncrystallizable. The sulphate of the binoxide of iridium is yellow, uncrystallizable, and soluble in water and alcohol, forming an orange solution not precipitated by the alkalis, but which gives, with chloride of barium, a precipitate of sulphate of barium, coloured brown by the binoxide.

§ XXXVIII. GLUCINUM.

GLUCINUM, GLYCIUM, or BERILLIUM, was first obtained in 1828, by Wöhler, by the action of potassium on *chloride of glucinum*. (See ALUMINUM.) It is a gray substance, having a slight metallic lustre, and very difficult of fusion. At common temperatures it is not acted on by air or water, but when heated in the air it burns into glucina: it burns vividly in oxygen gas, in chlorine, and in the vapour of iodine and bromine. It combines, with the evolution of heat and light, with sulphur, phosphorus, selenium, and arsenic. (WÖHLER, *Ann. de Ch. et Ph.*, 1828.) Its equivalent is doubtful: that deduced from the experiments of Berzelius is about 18, if glucina be considered as a protoxide; if glucina be regarded as a compound of 2 atoms of base and 3 of oxygen, then the equivalent 27 must be adopted, and its symbol will be (${}^2gl+{}^3o$); but till more is known of the analogies of this rare substance, it will be most convenient to assume glucina as a protoxide = ($gl+o$).

OXIDE OF GLUCINUM, or GLUCINA, ($gl+o$), was discovered in 1798, by Vauquelin, in the *beryl*: it also exists in the *emerald* of Peru, in *euclase*, in the *chrysoberyl*, in *phenakite*, and in a few other rare minerals. It is white, insipid, and insoluble in water; it has no action on vegetable colours; its specific gravity = 2.97. It dissolves in caustic potassa and soda, but not in ammonia, and thus resembles alumina, but differs from yttria. Again it differs from alumina, but resembles yttria, in being soluble, when freshly precipitated, in carbonate of ammonia; it is much more soluble in this solution than yttria. With the acids it forms saline compounds of a sweetish astringent taste, (hence the name, from *γλυκὺς*, *sweet*.) It is not precipitated by ferrocyanuret of potassium.

i. The *beryl*, or *aquamarine*, is found in primitive rocks in many parts of the world, but especially fine in Siberia. It is usually transparent, and pale-green or blue. It crystallizes in six-sided prisms.

ii. The *emerald* is principally found in Peru, crystallized in regular six-sided prisms, the edges or angles of which are sometimes replaced by facets. Its colour is green, and it is either transparent or translucent.

iii. *Euclase* is a very rare crystallized mineral, originally found in Peru, but has since been brought, in insulated crystals, from the Brazils.

iv. *Chrysoberyl*, or *Cymophane*, occurs most frequently in Brazil, where it accompanies topazes in alluvial soil; it has also been found in Ceylon and in Siberia; it is green, or yellow-green, and in one direction slightly opalescent; it occurs in rounded pieces and prismatic crystals. Specific gravity 3.7.

v. *Phenakite*. This mineral was discovered by Nordenskiöld mixed

with emerald from the Uralian Mountains; it had been mistaken for quartz, hence the above name, from $\phi\epsilon\nu\alpha\xi$, *deceiver*; it forms flat colourless rhomboids.

These minerals, analyzed by Vauquelin, Thomson, and Hartwall, are constituted as follows:—

	Beryl. (Vauquelin.)	Emerald. (Vauquelin.)	Euclase. (Vauquelin.)	Chrysoberyl. (Thomson.)	Phenakite. (Hartwall.)
Silica	68 . .	64.5 . .	44.33 . .	— . .	55.14
Alumina	15 . .	16.0 . .	31.83 . .	76.75 . .	—
Glucina	14 . .	13.0 . .	23.84 . .	17.79 . .	44.47
Oxide of chromium	— . .	3.0 . .	— . .	— . .	—
Oxide of iron	1 . .	— . .	— . .	4.50 . .	—
Lime	2 . .	1.5 . .	— . .	— . .	—
Water and loss	— . .	2.0 . .	— . .	0.96 . .	0.39
	100	100.0	100.00	100.00	100.00

To obtain glucina from either of these minerals, proceed as follows:—Reduce it to a fine powder, and fuse it with thrice its weight of hydrate or carbonate of potassa; dissolve the fused mass in dilute hydrochloric acid, and evaporate to dryness, by which the silica is rendered insoluble: digest this dry residue in water acidulated by hydrochloric acid, and add ammonia, which throws down a mixture of glucina and alumina; wash the precipitate, and digest it whilst moist in excess of carbonate of ammonia, by which the glucina is dissolved, and, on filtering, the alumina remains behind; then boil the filtered liquid, and carbonate of glucina is thrown down, which, washed, dried, and heated to redness, affords pure glucina. It consists of

	Berzelius.			
Glucinum 1	18	68.2	68.83	
Oxygen . 1	8	31.8	31.17	
Glucina 1	26	100.0	100.00	

CHLORIDE OF GLUCINUM is obtained by dissolving glucina in hydrochloric acid, and carefully evaporating to dryness out of the contact of air; or it may be procured by a process similar to that described for the chloride of aluminum, in which case it forms a silky sublimate, becoming brown when fused, and soluble in water. BROMIDE OF GLUCINUM, formed by the direct combination of its elements, sublimes in acicular crystals, fusible, and very soluble in water with the evolution of heat. IODIDE OF GLUCINUM resembles the bromide and chloride. FLUORIDE OF GLUCINUM: after perfect evaporation to dryness of a solution of glucina in hydrofluoric acid, the residue is soluble in water.

NITRATE OF GLUCINA is difficultly crystallizable, deliquescent, and soluble in alcohol.

SULPHURET OF GLUCINUM.—Glucinum burns brilliantly in sulphur vapour, forming a gray compound difficultly soluble in water, and evolving sulphuretted hydrogen with acids.

SULPHATE OF GLUCINA.—When glucina is dissolved in excess of sulphuric acid, evaporated till acid begins to escape, and then alcohol added, a crystallizable *bisulphate of glucina* separates, the solution of which dis-

solves carbonate of glucina, and becomes a *subsulphate*, which is not crystallizable, but which, after evaporation to dryness, is separated by the action of water into a *neutral sulphate*, and an insoluble salt containing great excess of base.

PHOSPHURET OF GLUCINUM.—Glucinum burns in the vapour of phosphorus as in that of sulphur, and produces a gray pulverulent phosphuret, which disengages phosphuretted hydrogen in water.

PHOSPHATE OF GLUCINA is precipitated in a gelatinous form when phosphate of soda is added to solution of chloride of glucinum: it fuses into a transparent glass.

SELENIURET OF GLUCINUM is formed as the sulphuret, and with the same phenomena.

CARBONATE OF GLUCINA falls in the form of a bulky flocculent precipitate, which is light and soft when dried; it is easily decomposed by heat.

CHARACTERS OF THE SALTS OF GLUCINA.—These salts are astringent and sweet: they are precipitated by the caustic fixed alkalis, and the precipitate is redissolved by their excess, and sparingly by their carbonates: it is not soluble in caustic ammonia, but readily so in carbonate of ammonia: they are not precipitated by ferrocyanuret of potassium. A characteristic property of glucina is, that when a warm solution is mixed with a warm solution of fluoride of potassium till a precipitate begins to appear, and the mixture then suffered to cool, a difficultly-soluble double salt separates in the form of lamellar crystals. (BERZELIUS.) Sulphate of glucina does not form a crystallizable double salt when mixed with sulphate of potassa.

§ XXXIX. ZIRCONIUM.

SIR H. DAVY first demonstrated the nature of *Zirconia*, and its metallic base was obtained by Berzelius in 1824 by acting upon the potasso-fluoride of zirconium by potassium. It is a black powder, having the appearance of plumbago, and not apparently conducting electricity. It is difficulty-soluble in the acids, with the exception of the hydrofluoric, which readily dissolves it, evolving hydrogen. Heated in the atmosphere, it burns into zirconia. Its equivalent, deduced from the analyses of Berzelius, is about 22, if zirconia be regarded as a protoxide; but if an equivalent of zirconia be assumed as containing 2 atoms of base and 3 of oxygen ($2Zir + 3O$), the equivalent will then be about 33. We shall for the present adopt the former atomic number.

OXIDE OF ZIRCONIUM. ZIRCONIA. ($Zir + O$) or ZIR, was discovered in 1789 by Klaproth: it is of rare occurrence, having only been found in the *Zircon* or *Jargon* (whence the name of this earth). The zircon is a *silicate of zirconia*; it is found in Ceylon, and occurs in some sienitic rocks: when colourless and transparent, it ranks among the gems:

when coloured brown or red, it is termed *hyacinth* or *jacinth*, which also occurs in Ceylon, and is found in small crystals in the sand of the rivers of that island; also near Pisa in Italy; in Brazil; and abundantly in the sands of the brook of Expailly in France (Dép. Haute Loire). These minerals contain about 70 per cent. of zircon, combined with silica and occasionally tinged by oxide of iron. (KLAPROTH, *Beiträge*.) Zirconia is obtained from them by the following processes:—Reduce the colourless zircons to a fine powder, having previously heated them to redness, and quenched them in water. Mix the powder with nine times its weight of hydrated potassa, and gradually project it into a red-hot silver crucible, and keep it in perfect fusion for two hours. When the crucible has cooled, reduce the mass to a fine powder, and boil it in distilled water. Boil the undissolved residue in hydrochloric acid; filter, and evaporate to dryness; redissolve the dry mass in distilled water, and precipitate by carbonate of soda. The carbonate of zirconia which falls may be decomposed by heat.

The following method of obtaining pure zirconia is recommended by Dubois and Silveira. (*Ann. de Ch. et Ph.*, xiv. 110.) Powder the zircons very fine, mix them with 2 parts of hydrated potassa, and heat them red-hot in a silver crucible for an hour. Treat the substance obtained with distilled water, pour it on a filter, and wash the insoluble part well; it will be a compound of zirconia, silica, potassa, and oxide of iron. Dissolve it in hydrochloric acid, and evaporate to dryness, to separate the silica. Redissolve the salts of zirconia and iron in water; and to separate the zirconia which adheres to the silica, wash it with weak hydrochloric acid, and add it to the solution. Filter the fluid, and precipitate the zirconia and iron by pure ammonia; wash the precipitate and treat it with a boiling solution of oxalic acid, which retains the iron, whilst an insoluble oxalate of zirconia is formed. It is then to be filtered, and the oxalate washed, until no iron can be detected in the water that passes. The oxalate of zirconia is, when dry, of an opaline colour; after being well washed, it is to be decomposed by heat in a platinum crucible. Thus obtained, the zirconia is perfectly pure, but is not affected by acids. It must be re-acted on by potassa as before, and then washed until the alkali is removed. Afterwards dissolve it in hydrochloric acid, and precipitate by ammonia. The hydrate thrown down, when well washed, is perfectly pure, and easily soluble in acids. (Other methods of proceeding are pointed out by Berzelius, *Lehrbuch*, i.)

Pure zirconia is a white infusible substance, insoluble in water, specific gravity 4.3. After having been heated to redness it scratches glass; it resists the action of the acids, with the exception of the sulphuric; and according to Berzelius, the best method of rendering it soluble consists in mixing it in fine powder with sulphuric acid diluted with its weight of water, and heating the whole in a platinum crucible till the acid is evaporated, but not to redness: the *sulphate of zirconia* thus obtained is soluble in hot water.

Hydrate of Zirconia may be thrown down from this solution by caustic ammonia in the form of a bulky gelatinous precipitate, which if dried, or even washed with boiling water, loses its easy solubility; when exposed to a red heat it becomes remarkably luminous after it has lost

its water. This hydrate is sparingly soluble in the alkaline carbonates, and consists of 2 atoms of zirconia and 1 of water; zirconia being composed of

					Berzelius,
Zirconium	1	. . . 22	. . . 73.3	. . .	73.686
Oxygen	. 1	. . . 8	. . . 26.7	. . .	26.314
<hr/>					
Zirconia	1	30	100.0		100.000

CHLORIDE OF ZIRCONIUM is obtained in the form of a white fixed compound, by heating zirconium in chlorine. Hydrated zirconia dissolves readily in hydrochloric acid, and the solution yields, on evaporation, small acicular silky crystals of *hydrated chloride*, soluble in water and in alcohol, but only sparingly soluble in hydrochloric acid. The anhydrous chloride cannot be obtained pure by heating the hydrate, for in that case it loses half its chlorine in the form of hydrochloric acid, whilst half the zirconium becomes zirconia.

FLUORIDE OF ZIRCONIUM.—Zirconia dissolves readily in hydrofluoric acid, and yields, by slow evaporation, a crystallized salt, which, by the action of water, is resolved into a sub and super salt. When solution of fluoride of potassium is added to excess of fluoride of zirconium, the solution yields, on evaporation, small granular crystals, sparingly soluble in cold water, of *potassofluoride of zirconium*, consisting, according to Berzelius, of

Potassium 1	. . . 40	. . . 29
Zirconium 2	. . . 44	. . . 32
Fluorine 3	. . . 54	. . . 39
<hr/>			
Potassofluoride of zirconium	1	138	100

When solution of fluoride of zirconium is dropped into excess of fluoride of potassium, an analogous triple compound is formed, containing 2 atoms of potassium, 3 of zirconium, and 5 of fluorine. (BERZELIUS.)

NITRATE OF ZIRCONIA is a very soluble and uncrystallizable compound: its solution dissolves hydrate of zirconia, and it is only imperfectly decomposed by the addition of alkalis.

SULPHURET OF ZIRCONIUM is formed by heating sulphur and zirconium in an exhausted vessel, or in an atmosphere of hydrogen; in both cases light is emitted, and a pulverulent brown sulphuret formed. It is insoluble in nitric, hydrochloric, and sulphuric acid, feebly acted on by nitrohydrochloric acid, but dissolved and decomposed by hydrofluoric acid.

SULPHATE OF ZIRCONIA. ($\text{ZIR} + \text{S}'$).—This salt is formed by digesting zirconia with sulphuric acid and a little water; the mixture must be boiled to dryness, and ultimately heated nearly to redness; the remaining sulphate is readily soluble in boiling water, and yields, on evaporation, a gum-like mass, with no traces of crystallization; but if it be redissolved in sulphuric acid, the solution yields crystals which are still a neutral sulphate, and which may be freed from adhering acid by washing with alcohol; they contain water of crystallization. Berzelius has also

described a *disulphate*, a *tris-sulphate*, an *ammonia-sulphate*, and a *potassa-sulphate of zirconia*.

PHOSPHATE and CARBONATE OF ZIRCONIA are insoluble salts.

CHARACTERS OF THE SALTS OF ZIRCONIA.—These salts have an astringent taste: they are precipitated by caustic potassa, and the precipitate is not soluble in excess of the alkali. When boiled with sulphate of potassa a subsalt of zirconia subsides. Infusion of galls produces in them a yellow precipitate, and phosphate of soda throws down a white phosphate of zirconia. The recently-precipitated carbonate of zirconia is soluble in excess of bicarbonate of ammonia, or of potassa.

§ XL. YTTRIUM.

IN 1794, Professor Gadolin discovered a new earth in a mineral from the quarry of Ytterby, in Sweden, to which Ekeberg, in 1797, gave the name of *Yttria*. The mineral has since been termed *Gadolinite*. It is composed of yttria, silica, and the oxides of iron and cerium. The following process for obtaining pure yttria is described by Vauquelin. (*Ann. de Ch.*, xxxvi. 150.)

Fuse pulverized *Gadolinite* with twice its weight of potassa; wash the mass with boiling distilled water, and filter. The filtered solution, which has a beautiful green colour, yields, during evaporation, a black precipitate of oxide of manganese. When this has ceased to appear, allow the liquor to stand; decant the clear part, and saturate with nitric acid. Let the insoluble part be also digested with extremely dilute nitric acid, which will take up the soluble earths only, and will leave undissolved the silica and oxide of iron. Let the two portions be mingled together; and evaporated to dryness; then redissolved and filtered; by which means any remains of silica and oxide of iron are separated. To obtain the yttria from the nitric solution, it would be sufficient, if no other earth were present, to precipitate it by carbonate of ammonia; but small portions of lime, and of oxide of manganese, are still present along with it. The first is separated by a few drops of carbonate of potassa; and the manganese, by the cautious addition of hydrosulphuret of potassa. The yttria is then to be precipitated by pure ammonia, washed abundantly with water, and dried. It amounts to about 35, or, according to Berzelius, 45 per cent. of the weight of the stone. It has been found also to form about one-fifth of the weight of *ytrotantalite*, and about one-twelfth of that of *ytrocerite*; and it occurs in the minerals termed *Orthite* and *Pyrrorthite*, and in the *fluoride* and *phosphate of yttrium*. (See COLUMBIUM.)

Berzelius obtains yttria as follows:—*Gadolinite* in fine powder is dissolved in nitrohydrochloric acid, and the solution decanted from the deposited silica: crystals of sulphate of potassa are then added to it, and it is left for 24 hours; in proportion as the fluid becomes saturated by the sulphate, a white or yellowish powder falls, which is a double sulphate of potassa and protoxide of cerium: this is separated, and the clear solution neutralized by caustic ammonia, and the oxide of iron thrown down by succinate of ammonia. The precipitate is separated by filtration, and the

clear liquid precipitated by caustic ammonia, by which yttria (with a little oxide of manganese) is thrown down: the oxide of manganese may be separated by digesting this precipitate in a solution of carbonate of ammonia, filtering, and boiling, by which carbonate of yttria separates: this, being dried and heated to redness, leaves yttria.

Wöhler obtained *yttrium* in 1828 by dissolving yttria in hydrochloric acid, evaporating to dryness, and acting upon the *chloride of yttrium* so obtained by potassium: by washing the residue of this action, the yttrium remains in the form of gray metallic scales, brittle, and resisting the action of air and water: when heated in air or oxygen it burns brilliantly into yttria, which shows slight marks of fusion; it dissolves in sulphuric acid and in solution of potassa, but not in ammonia: it combines with sulphur, selenium, and phosphorus. (*Phil. Mag. and Ann.*, v. 393.) The equivalent of yttrium is probably 32.

OXIDE OF YTTRIUM. (*yt + o*) or Yt.—Yttria is insipid, white, and without action on vegetable colours. Its specific gravity = 4.842. It is insoluble in water, but very retentive of it: insoluble in pure alkalis, but readily soluble in carbonated alkalis. In carbonate of ammonia it is much less soluble than glucina. It forms salts which have a sweetish austere taste, and which have been little examined. They are decomposed by the pure alkalis, and by lime and baryta. Oxalic acid and oxalate of ammonia throw down a white curdy precipitate from the solutions of yttria. Ferrocyanuret of potassium occasions in them a gray granular precipitate; phosphate of soda, a white gelatinous one; and tincture of galls throws down brown flocculi.

Yttria appears to consist of

						Berzelius.		
Yttrium	1	.	.	32	.	80	.	80.1
Oxygen	1	.	.	8	.	20	.	19.9
Yttria	1			40		100		100.0

CHLORIDE OF YTTRIUM is very soluble, and deliquescent. When yttrium is heated in chlorine, it burns brilliantly, and the resulting chloride sublimes in white acicular crystals.

IODIDE AND BROMIDE OF YTTRIUM.—Yttrium burns when heated in the vapour of iodine or bromine; the resulting compounds are volatile, and form crystalline sublimates, fusible, and soluble in water with the evolution of heat.

FLUORIDE OF YTTRIUM is an insoluble compound; it occurs *native*, combined with the fluorides of cerium and calcium, in the vicinity of Fahlun.

SULPHURET OF YTTRIUM.—Yttrium burns in sulphur-vapour, and produces a pulverulent gray sulphuret, insoluble in water, and evolving sulphuretted hydrogen when acted on by acids.

SULPHATE OF YTTRIA is crystallizable and of a pale-pink hue; it is remarkable for its tardy solubility in water. It forms a double salt with sulphate of potassa.

SELENIURET OF YTTRIUM.—Yttrium combines with selenium with

feeble ignition, when they are fused together; the compound is black and does not decompose water; but on the addition of an acid, yields seleniuretted hydrogen.

NITRATE OF YTTRIA is deliquescent, but by spontaneous evaporation it may be obtained in colourless crystals.

PHOSPHURET OF YTTRIUM.—Yttrium burns in the vapour of phosphorus, and produces a pulverulent gray phosphuret, which decomposes water with the evolution of phosphuretted hydrogen.

PHOSPHATE OF YTTRIA.—The neutral phosphate is insoluble, and fusible before the blowpipe. When it is dissolved in an acid, and precipitated by ammonia, a basic phosphate falls. A *native phosphate of yttria* occurs near Lindesness, in Norway. (See Berzelius, in respect to some peculiarities of this salt.)

CARBONATE OF YTTRIA is a light flocculent precipitate, sparingly soluble in excess of carbonic acid, and in the carbonated alkalis. It decomposes and slowly dissolves in the salts of ammonia: dissolved in carbonate of ammonia it affords a crystallizable *ammonio-carbonate of yttria*.

CHARACTERS OF THE SALTS OF YTTRIA.—They have a sweet astringent taste, not unlike those of glucina: their specific gravity exceeds that of the other earthy salts: some of them, when crystallized, have an amethystine tint, derived probably from a trace of manganese. They are thrown down of a white colour by ferrocyanuret of potassium, and by caustic potassa, and the precipitate is not soluble in excess of the precipitant. Carbonated alkalis, when added in excess, slowly redissolve the precipitate. The *sulphate* is the most characteristic salt.

§ XLI. THORINUM.

THIS substance was discovered by Berzelius in 1828, in a rare and complex mineral, found in the syenitic rock of the Isle of Lovon, near Brevig, in Norway. It contained about 58 per cent. of *thorina*, (*Poggend.*, xvi. 387,) which was obtained as follows: the mineral in powder was digested in hydrochloric acid, which formed a gelatinous mass, which, evaporated to dryness, and digested in dilute hydrochloric acid, left silica. The hydrochloric solution was then freed from lead and tin, by a current of sulphuretted hydrogen, and the clear solution saturated by ammonia: this occasioned a precipitate, which was washed, dissolved in dilute sulphuric acid, and the solution evaporated to a small bulk; during this evaporation *sulphate of thorina* was deposited, which, being washed with a saturated solution of sulphate of potassa, was dissolved in boiling water, and decomposed by caustic potassa, which threw down the thorina in the state of a white powder. (*Ann. de Ch. et Ph.*, xliii. 5.)

By passing a current of dry chlorine over a mixture of thorina and charcoal-powder, a crystalline *chloride of thorinum* is obtained, which is easily decomposed by potassium, and the product is *thorinum*. It is of a gray colour, metallic lustre, and apparently malleable. It is not oxidized by hot or cold water, but when heated in the air it burns with great

brilliancy into thorina, which is snow-white, and shows no traces of fusion. It is feebly acted on by sulphuric acid, and scarcely by nitric acid: it is not attacked by the caustic alkalis at a boiling heat. Hydrochloric acid dissolves it, with the evolution of hydrogen. Its apparent equivalent is 60. (59.6 TURNER.)

OXIDE OF THORINUM. THORINA ($th + o$), obtained as above described, and after having been heated to redness, is white, and insoluble in the acids, with the exception of the sulphuric. When thrown down in the state of *hydrate* it dissolves readily, and exposed to the air absorbs carbonic acid. It probably consists of

Thorinum	1	.	.	60	.	.	88
Oxygen	1	.	.	8	.	.	12
							<hr/>
Thorina	1			68			100

Thorinum combines energetically with chlorine, sulphur, and phosphorus. The *chloride* has been above adverted to: the other compounds have been but imperfectly examined.

Thorina is distinguished from the other oxides by the following properties: from alumina and glucina, by its insolubility in pure potassa; from yttria, by forming with sulphate of potassa a double salt, which is quite insoluble in a cold saturated solution of sulphate of potassa; from zirconia, by the circumstance that this earth, after being precipitated from a hot solution of sulphate of potassa, is almost insoluble in water and the acids. Thorina is precipitated also by ferrocyanuret of potassium, which does not separate zirconia from its solutions. Berzelius has remarked that sulphate of thorina is much more soluble in cold than in hot water, so that a cold saturated solution becomes turbid when heated, and in cooling recovers its transparency. (TURNER'S *Elements*.)

§ XLII. ALUMINUM.

THE term *aluminum* or *aluminium* has been applied to the metallic base of the earth *alumina*, a substance of common occurrence in the mineral world, and of great importance in its applications to the arts. The nature of alumina was discovered by Davy in 1808, (*Elem. Chem. Phil.*, 355,) who found that potassa was generated by passing the vapour of potassium over white-hot alumina: he did not, however, determine the properties of its base. This has since been more accurately effected by Wöhler, to whom we owe the following ingenious method of obtaining it. (*Ann. de Ch. et Ph.*, Jan. 1828, and *Poggendorff, Annalen*, xi. 146.) *Chloride of aluminum* is heated with potassium in a small platinum or porcelain crucible: the heat of a spirit-lamp is sufficient, for when the substances begin to act, the temperature suddenly rises to redness, and care should be taken so to adjust the relative proportions of materials, that none of the chloride may be evaporated in an undecomposed state, while at the same time there should not be excess of alkali in the residue. When the crucible is cold, its contents are well-washed with cold water, by which a finely-divided gray substance, with a certain degree of metallic lustre, is obtained, which is pure aluminum.

Aluminum is extremely difficult of fusion; and although in the pulverulent state it does not apparently conduct electricity, it becomes a conductor when its particles are aggregated by heat. This, if not arising from imperfect contact, is an interesting fact, and holds good also, according to Wöhler, in the case of iron, which does not conduct when in very fine powder. Aluminum is not oxidized by exposure to air, but, when heated nearly to redness, it burns into a hard white substance, having the properties of alumina. When sprinkled into the flame of a spirit-lamp it scintillates like iron-filings, and if, when red-hot, it be immersed in oxygen, it burns with vivid light and intense heat: the result is fused alumina, apparently as hard as corundum.

Aluminum is not acted on by water at common temperatures, but when boiled it is slightly oxidized, and a little hydrogen is evolved: the oxidizement is, however, imperfect and superficial. It is not affected by nitric or sulphuric acids at common temperatures, but it rapidly dissolves in hot sulphuric acid, and sulphurous acid is evolved. The dilute acid dissolves it with the evolution of hydrogen, as is also the case with hydrochloric acid. It is soluble with the evolution of hydrogen in the caustic alkalis, and alkaline solutions of alumina are the results.

There is much difficulty in determining the equivalent of aluminum, arising out of the different views that may be taken of the atomic constitution of *alumina*, which is its only known oxide: some chemists regard it as a *protoxide*, and in that case a number intermediate between 9 and 10 would represent aluminum; others, from the analogy that subsists between some of the combinations of alumina and the peroxide of iron, have regarded it as a *sesquioxide*; and here again a discrepancy in its equivalent ensues, dependent upon its being considered as composed of 1 aluminum and 1.5 oxygen, or of 2 and 3. Gmelin has adopted the equivalent 9, and Thomson 10, regarding alumina as a *protoxide*: Dr. Turner, considering alumina as a *sesquioxide*, represents aluminum by the equivalent 13.7, and then doubles that number in order that alumina may be regarded as consisting of 2 equivalents of aluminum and 3 of oxygen. I shall assume 26 as the equivalent weight of an atom of aluminum, and shall consider alumina as $= (al + 3o)$.

OXIDE OF ALUMINUM. SESQUIOXIDE OF ALUMINUM. ALUMINA. $(al + 3o)$ or AL.—To obtain pure *alumina*, we decompose a solution of pure *alum* by excess of carbonate of potassa, wash the precipitate with repeated portions of hot distilled water, redissolve it in hydrochloric acid, precipitate it again by ammonia, thoroughlyedulcorate, and dry the precipitate: it is rendered anhydrous by exposure to a red heat. In this process, the alumina which first falls always retains a little potassa, which is got rid of by the second solution, and precipitation by ammonia: if ammonia be used as the original precipitant of a solution of *alum*, the resulting precipitate retains subsulphate of alumina, not decomposable by excess of ammonia. Pure alumina may also be obtained, according to Gay Lussac (*Ann. de Ch. et Ph.*, v. 102), by igniting *ammonia alum*, previously deprived of water of crystallization by heat: sulphate of ammonia evaporates, and alumina remains, perfectly white, and very soft to the touch, but nevertheless, almost insoluble in acids. It readily blends with water, but

assumes its former properties after having been gently heated. Its extreme division, and the hardness of its particles, observes Gay Lussac, might render it useful for polishing metal, and its whiteness for the preparation of colours.

Alumina is a colourless, insipid, infusible, and insoluble powder, without action upon vegetable blues: its specific gravity is 2. It has a strong attraction for moisture, which it rapidly absorbs from humid air to the amount of one-third its own weight. When precipitated from its solution, and dried at a temperature of 60° , it retains about half its weight of water; this may be expelled by ignition. When mixed with water, alumina is characterized by the plasticity of the mixture; and if the paste be dried in the air, and then heated, it shrinks considerably in consequence of the loss of water; this shrinkage was applied by Wedgwood to pyrometrical purposes (p. 151). Alumina has a strong affinity for various organic compounds, and its use in the arts of dyeing and calico-printing depends upon its attraction for different colouring-principles, and for ligneous fibre. If ammonia be added to a solution of alum in infusion of cochineal, or of madder, the aluminous earth falls in combination with the red colouring-matter, and the supernatant liquor remains colourless. Colours thus prepared are called *Lakes*.

Moist alumina is readily soluble in most of the acids; but after the expulsion of its water by a red heat, it is much more difficultly dissolved, or even insoluble. It is very sparingly soluble (when moist) in caustic ammonia; but potassa and soda readily dissolve it, and it is also soluble, to a certain extent, in the aqueous solutions of baryta and strontia. The fixed alkaline solutions of alumina are decomposed by the acids and by ammoniacal salts. Some of the earthy combinations of alumina exist *native*, and in them it has been regarded as performing the part of an acid; so that they have been called *Aluminates*. Alumina is recognised by its solubility in caustic potassa; by the formation of octoëdral crystals of alum on evaporating its sulphuric solution with the addition of sulphate of potassa; and by the fine blue colour which it affords when moistened with nitrate of cobalt and strongly heated: this, according to Berzelius, is the most certain test.

Alumina, in reference to the above-mentioned equivalent, will consist of

				Berzelius.	Davy.
Aluminum	1	26	52	53.3	56
Oxygen	3	24	48	46.7	44
Alumina	1	50	100	100.0	100

Native Alumina may be said to constitute the *sapphire*, which occurs either colourless or pale-blue, is extremely hard, and occasionally crystallized: its specific gravity is about 4. The oriental *ruby* and the oriental *topaz* are red and yellow varieties of sapphire. These gems are mostly found in alluvial deposits in Ceylon and Pegu: they have also been met with in France and Bohemia. *Corundum*, *adamantine spar*, and *emery*, are minerals also consisting chiefly of alumina, with less than 2 per cent. of oxide of iron, and a little silica. All these substances are extremely hard, being, in that respect, second only to diamond.

HYDRATES OF ALUMINA.—When alumina is precipitated from its solutions in the state of hydrate, washed, and dried at between 70° and 80° , it always contains about 59 per cent. of water, although its physical characters vary considerably, dependant upon the strength of the solution from which it has been precipitated: if from a saturated solution of alum, it forms a friable, opaque, spongy mass; if from a dilute solution, a transparent, yellowish, gum-like, or gelatinous substance, which has no earthy characters, and does not adhere to the tongue. The composition of these hydrates, dried below 80° , is

Alumina	1	50	41
Water	8	72	59
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Octohydrate of alumina	1	122	100

Exposed to a red heat, the *gelatinous* hydrate loses only about 43 per cent. of its water, and the residue, under these circumstances, consists of

Alumina	1	50	73.5
Water	2	18	26.5
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Bihydrate of alumina	1	68	100.0

By a protracted white heat, a further portion of water to the amount of about half an atom may be expelled, and the residuary hydrate then contains about 20 per cent. of water.

The pulverulent or spongy hydrate of alumina, unlike the foregoing, loses the whole of its water at a red heat, and hence, in analyses, it is always desirable that the alumina should be thrown down in the spongy and not in the gelatinous state, as in the latter case a considerable error in the estimation of its quantity might ensue. The gelatinous alumina may, however, be brought to the state of the spongy, by moistening it with sulphuric acid and then giving it a red heat; both the water and the acid are then entirely driven off.

Native Hydrate of Alumina constitutes the mineral called *Gibbsite*, from Richmond in Massachussets: it occurs in small stalactitic aggregates of a fibrous texture, and of a greenish-white colour: its density is 2.4, and it contains about 35 per cent. of water. According to Mitscherlich, a corresponding hydrate may be artificially formed by digesting excess of recently-precipitated hydrate of alumina in a solution of caustic potassa, at a moderate temperature, and either preserving the filtered solution in a well-closed flask, or suffering it slowly to absorb carbonic acid from the air; in each case, small white translucent crystals are formed, which contain about 35 per cent. of water, not expelled at 212° . *Gibbsite*, therefore, and these crystals, are composed of

Alumina	1	50	65
Water	3	27	35
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Terhydrate of alumina	1	77	100

The mineral called *Diaspore*, (from its property of decrepitating into powder when heated,) is a native bihydrate of alumina.

CHLORIDE OF ALUMINUM. (*al+3c.*)—This compound has been mentioned as a source of *aluminum*: it was obtained by Wöhler, as follows:—Alumina, in the state of pulverulent hydrate, is mixed into a

paste with powdered charcoal, oil, and sugar, and this is heated in a covered crucible till the organic matter is decomposed: an intimate mixture of the alumina with charcoal is thus obtained, which is introduced whilst hot into a proper porcelain or glass tube, placed in a convenient furnace: dried chlorine is then passed through it into a receiver attached to the other end of the tube, and the air being thus expelled, the tube is heated red-hot, and chlorine gradually passed into it: carbonic oxide is disengaged, and chloride of aluminum formed, which chiefly collects within the tube, and ultimately plugs it up. It is a crystalline translucent substance of the colour of chlorine; it fumes and deliquesces when exposed to air, and is energetically acted upon by water: it may be preserved in naphtha. If a solution of alumina in hydrochloric acid be evaporated to dryness, a hydrated chloride remains, which, at a higher temperature, evolves hydrochloric acid, and leaves alumina, so that chloride of aluminum cannot be thus obtained. The components of this chloride are

Aluminum	1	26	19.4
Chlorine	3	108	80.6
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Chloride of aluminum	1	134	100.0

This chloride combines with ammonia, and with sulphuretted and phosphuretted hydrogen: the *ammonio-chloride* has the formula ($al + 3c$) $+ 3(n + 3h)$.

CHLORATE OF ALUMINA is a deliquescent salt.

IODIDE OF ALUMINUM ($al + 3i$) has not been obtained in the solid state, but exists in solution when gelatinous alumina is dissolved in hydriodic acid.

BROMIDE OF ALUMINUM ($al + 3b$) was obtained by D'Arcet, by the action of bromine at a high temperature upon a mixture of alumina and charcoal; in its principal properties it resembles the chloride.

FLUORIDE OF ALUMINUM.—Hydrate of alumina readily dissolves in hydrofluoric acid, and, on evaporation, a gummy substance is obtained, which bears a red heat without entire decomposition. Berzelius has described two *alumino-fluorides of potassium* obtained from mixed solutions of the two fluorides. *Alumino-fluoride of sodium* occurs native in *Kryolite*, a rare mineral hitherto found only in Greenland.

NITRATE OF ALUMINA is very difficultly crystallizable, and generally obtained, on evaporating its solution, in the form of a semitransparent gum-like mass, very deliquescent, and soluble in alcohol: it may be obtained by a very careful evaporation in soft foliated crystals. When decomposed by caustic ammonia, a pasty precipitate separates, which is a *subnitrate*, not decomposed by excess of ammonia. (BERZELIUS.)

SULPHURET OF ALUMINUM ($al + 3s$) is obtained by dropping sulphur upon incandescent aluminum, or by passing the vapour of sulphur over red-hot aluminum. A black compound is the result, which is decomposed by exposure to air, and which, when thrown into water, deposits alumina, and evolves sulphuretted hydrogen. When an aluminous salt is decomposed by an alkaline hydrosulphuret, alumina is thrown down, and sulphuretted hydrogen is evolved.

HYPOSULPHITE OF ALUMINA.—No precipitate falls when oxalate of alumina is added to hyposulphite of lime. (HERSCHEL.)

SULPHITE OF ALUMINA is insoluble in water; it dissolves in sulphurous acid, and the solution soon passes into sulphate: it is decomposed by heat. (FOURCROY.)

HYPOSULPHATE OF ALUMINA was obtained by Heeren, by mixing solutions of hyposulphate of baryta and sulphate of alumina; but on evaporating the filtered solution in vacuo, a white mass was obtained, the solution of which was copiously precipitated by chloride of barium, so that a dry hyposulphate of alumina cannot be obtained. (Poggendorff, vii. 180.)

SULPHATE OF ALUMINA ($Al + 3S'$) is formed by digesting hydrate of alumina in sulphuric acid diluted with an equal bulk of water: the solution is evaporated and alcohol added, which throws down the sulphate. It dissolves in 2 parts of water, and forms small crystals, of a sweet and astringent taste. When excess of hydrated alumina is boiled in the diluted acid, and the solution filtered and evaporated in vacuo over sulphuric acid, it congeals into a soft, white, semitransparent mass, which may be dried on blotting paper, and is not altered by the air. Exposed to heat, this salt loses water of crystallization, and an *anhydrous sulphate* remains. By long exposure to a red heat, the whole of the acid is expelled. The solution of this salt may be used as a test for potassa; for when it is dropped into a strong solution of that alkali or its salts, small crystalline grains of alum are thrown down. It consists of

Alumina	1	50	29.4
Sulphuric acid	3	120	70.6
Anhydrous sulphate of alumina	1	170	100.0

The crystallized salt contains

Alumina	1	50	15.1	} 51.3
Sulphuric acid	3	120	36.2	
Water	18	162	48.7	
Crystallized sulphate of alumina	1	332	100.0	100.0

This sulphate is found native in the volcanic island of Milo, in the Archipelago.

SUBTRISULPHATE OF ALUMINA. ($Al + S'$) + 9 *q*, or ($3Al + 3S'$) + 27 *q*.—When ammonia is added to a solution of sulphate of alumina, a white powder falls, which is not decomposed by excess of ammonia, and which consists of

Alumina	1	50	29.3
Sulphuric acid	1	40	23.4
Water	9	81	47.3
Subsulphate of alumina	1	171	100.0

This compound, in the preceding state of hydration, exists *native*, forming the mineral called *Aluminite*, or *Websterite*: it occurs near New-haven on the coast of Sussex; at Halle in Germany; at Bernon near

Eprenay; and at Auteuil near Paris: its usual geological position is the plastic clay immediately upon chalk.

OCTOBASIC SULPHATE OF ALUMINA. ($3\text{AL} + 3\text{S}'$).—When a solution of alum is decomposed by acetate of lead, the filtered solution, when heated to about 212° , becomes turbid, and deposits a white powder, which on cooling is redissolved: the same result is obtained, on mixing solutions of alum or of sulphate of potassa with pure acetate of alumina. This precipitate contains, according to Koechlin Schouch,

Alumina	8 . .	400 . .	77
Sulphuric acid	3 . .	120 . .	23
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Octobasic sulphate of alumina	1	520	100

SULPHATE OF ALUMINA AND POTASSA. COMMON ALUM. POTASH ALUM. ($\text{AL} + 3\text{S}' + (\text{P} + \text{S}') + 24\text{q}$).—This useful salt is manufactured upon an extensive scale in Britain. *Aluminous slate*, which is an argillaceous slaty rock containing sulphuret of iron, is roasted so as to oxidize the iron and acidify the sulphur: on lixiviating the roasted ore, a *sulphate of alumina* is obtained, which, with the addition of *sulphate of potassa*, yields alum. The *shales* or wastes of old coal-mines, which fall down in a decaying or decomposing state, yield, on lixiviation, considerable quantities of sulphate of alumina and sulphate of iron: the solution of these salts is evaporated at the alum-works, near Glasgow, in large brick cisterns, by carrying the flue of a furnace over its surface, and, when sufficiently concentrated, is run out into coolers, where the sulphate of iron crystallizes, and the sulphate of alumina, being the much more soluble salt, remains in the mother-liquors: to these, when heated, sulphate or chloride of potassium is added, and they then yield crystals of alum, not at first pure, but rendered so, and obtained in beautifully-perfect octoëdral crystals, by recrystallization. The sulphate of potassa, required for this manufacture, is obtained by burning common sea-weed, collected upon the coast; the ash, or *kelp*, contains salts of potassium, which are purified by crystallization: the mother-liquors, which were formerly thrown away, are now resorted to as sources of *iodine* (p. 371).

There are many other methods of manufacturing alum, such as by the decomposition of clay by sulphuric acid, and by the lixiviation of certain *alum stones*, as they are called, which are products of the joint action of sulphurous acid and oxygen upon volcanic rocks containing alumina and potassa; these abound in the Solfaterra, near Naples, and yield what is termed *Roman alum*: it differs from common alum in crystallizing in opaque cubes, and appears to contain more alumina than common octoëdral alum: when this variety is dissolved in cold water and slowly crystallized, it reappears in cubic crystals; but if dissolved in water heated to 110° , or higher, a subsulphate of alumina falls, and octoëdral alum is obtained. Roman alum has not been accurately analyzed.

Octoëdral alum has a sweet and astringent flavour, accompanied by some degree of acidity; its density is 1.71: it reddens vegetable blues: it dissolves in about 15 parts of cold water, and in about its own weight of boiling water (18.5 cold and 0.75 boiling water, GRAHAM). The crystals, when heated, readily fuse in their water of crystallization, and

when this is expelled by the application of a sufficient temperature, the dry alum becomes opaque and spongy, and in this state is generally termed *roche alum*, or when further dried, *burnt alum*. At a red heat alum first loses that portion of its acid belonging to the alumina, and ultimately the sulphate of potassa is itself decomposed under the influence of the alumina, which combines with the potassa and displaces the sulphuric acid. In its *crystallized* state, alum consists of

Sulphate of alumina	1	170	35.8
Sulphate of potassa	1	88	18.6
Water	24	216	45.6
Crystallized alum	1	474	100.0

Or,

				Berzelius.	Thomson.
Alumina	1	50	10.6	10.76	11.09
Potassa	1	48	10.1	9.95	9.86
Sulphuric acid	4	160	33.8	33.74	32.85
Water	24	216	45.5	45.55	46.20
	1	474	100.0	100.00	100.00

"If the quantity of carbonate of soda necessary to neutralize a portion of alum be divided into three equal portions, and added in a gradual manner to the aluminous solution, it will be found that the alumina first precipitated is redissolved upon stirring, and that no permanent precipitate is produced till nearly 2 parts of alkaline carbonate are added. It is in the condition of this partially-neutralized solution that alum is generally applied as a mordant to cloth. Animal charcoal readily withdraws the excess of alumina from this solution, and so does vegetable fibre, probably from a similar attraction of surface. When this solution is concentrated by evaporation, alum crystallizes from it, generally in the cubic form, and the excess of alumina is precipitated." (GRAHAM.)

HOMBERG'S PYROPHORUS.—When potash alum is ignited with charcoal, a spontaneously-inflammable compound results, which has long been known under the name of *Homberg's pyrophorus*. The potassa is decomposed in this process, along with the acid of the alum, and pyrophorus is probably a compound of sulphur, charcoal, and potassium, with alumina. Pyrophorus is most successfully prepared by the following process. Mix equal parts of honey, or of brown sugar and powdered alum, in an iron ladle, melt the mixture over a fire, and keep it stirred till dry: reduce the dry mass to powder, and introduce it into a green glass phial coated with clay, and placed in a crucible of sand. Give the whole a red heat, and when a blue flame appears at the neck of the phial, allow it to burn about five minutes; then remove it from the fire, stop the phial, and allow it to cool, taking care that air cannot enter it. (See SULPHATE OF POTASSA.)

SULPHATE OF ALUMINA AND AMMONIA. AMMONIA ALUM. ($AL + 3S'$) + ($A + S'$) + $24Q$.—This salt is obtained exactly as the preceding, only *sulphate of ammonia* is substituted for sulphate of potassa: its atomic constitution also resembles that of potash alum, and it is so similar in other respects, that as far as mere appearance and more obvious properties

are concerned, the two salts are not readily distinguished. It is recognised by evolving ammonia, when triturated with lime or potassa. This variety of alum was formerly much in use, and the requisite ammonia was chiefly derived from putrid urine. When heated it loses water, then ammonia, and, at a very high heat, its acid, the residue being pure alumina.

SULPHATE OF ALUMINA AND SODA. **SODA ALUM.** $(\text{Al} + 3\text{S}') + (\text{S} + \text{S}') + 24\text{q}$.—In this salt *sulphate of soda* takes the place of the sulphate of potassa in the common alum: it crystallizes in octoëdra, which are less hard and regular than those of potash alum, and effloresce in a dry air. (*Quart. Jour.*, viii. 386.) It dissolves in about its own weight of water.

SULPHATE OF ALUMINA AND IRON.—This salt, formerly called *plumose alum*, forms white silky crystals or fibres, of a strong styptic taste, extremely fusible and soluble, and when heated evolving water, sulphuric acid, sulphurous acid, and oxygen, and leaving alumina and peroxide of iron. The atomic constitution of this salt has not been established; it has been analyzed by Klaproth (*Beiträge*), Berthier (*Ann. des Mines*, v. 259), and R. Phillips (*Ann. of Phil.*, 2nd series, v. 446), with the following results.

	Klaproth.	Berthier.	R. Phillips.
Protoxide of iron	7.50 . . .	12.0 . . .	20.7
Alumina	15.25 . . .	8.8 . . .	5.2
Sulphuric acid }	77.25 . . .	34.4 . . .	30.9
Water	44.0 . . .	43.2	43.2
	100.00	99.2	100.0

An octoëdral salt resembling alum, is formed from a mixed solution of sulphate of alumina and persulphate of iron. (MITSCHERLICH.)

Some other double salts of alumina (subsals) have been described by Riffault. (*Ann de Chim.*, xvi. 355.)

PHOSPHURET OF ALUMINUM is formed by passing the vapour of phosphorus over red-hot aluminum. Exposed to air it smells of phosphuretted hydrogen, and it decomposes water. (WÖHLER.)

PHOSPHATE OF ALUMINA precipitates when phosphate of soda is added to solution of alum; it is insoluble in water, but dissolves in phosphoric acid, and yields, on evaporation, a gummy deliquescent compound. When excess of ammonia is added to an acid solution of this phosphate, a *subphosphate of alumina* is precipitated, which is soluble in caustic potassa, and the formula of which is $(4\text{Al} + 3\text{p}')$. The mineral called *wavellite* is a *hydrated subphosphate of alumina*, with fluoride of aluminum. The rare mineral, called *ambligonite*, found at Chirnsdorff, in Saxony, is a double *phosphate of alumina and lithia*. (BERZELIUS.)

SELENIURET OF ALUMINUM is a black pulverulent compound, rapidly decomposed by water.

CARBONATE OF ALUMINA.—The precipitate thrown down by alkaline carbonates from a solution of alum is a compound of alumina and the carbonate employed. Water saturated by carbonic acid dissolves alumina,

but exposure to air destroys the combination; so that no carbonate of alumina exists. (SAUSSURE, *Jour. de Phys.*, lii. 28.)

SULPHOCYANURET OF ALUMINUM crystallizes in octoëdra, which are persistent in the air. (GRAHAM.)

BORATE OF ALUMINA may be formed by boiling recently-precipitated alumina with boracic acid: it is uncrystallizable, and of a very astringent taste.

ARSENATE OF ALUMINA.—This salt may be obtained by mixing solutions of alum and arseniate of soda; it is a white powder, insoluble in water, but soluble in arsenic acid.

ALLOYS OF ALUMINUM.—Aluminum probably exists in some of the varieties of cast-iron and steel. By fusing highly-carburetted steel with alumina, a peculiar alloy results, which is white, granular, and brittle, and which yields, on analysis, 6·4 per cent. alumina. On fusing 67 parts of this alloy with 500 of steel, a compound is obtained, which possesses all the characters of the best Bombay *wootz*, and like it, when its surface is polished and washed over with dilute sulphuric acid, exhibits the striated appearance called *damask*, for which the celebrated sabres of Damascus are remarkable, and which renders it probable that they also are made of *wootz*. (*Quarterly Journal of Science and Arts*, ix.)

CHARACTERS OF THE SALTS OF ALUMINA.—These salts have an astringent, sweet, and subacid taste: they are precipitated by the caustic fixed alkalis, but the precipitate is redissolved when they are added in excess. Sulphate of potassa, with a little sulphuric acid, added to a strong solution of alumina, throws down a white crystalline powder, which is *alum*: phosphate of soda produces a white flocculent precipitate of phosphate of alumina. Succinate of ammonia and infusion of galls occasion precipitates in strong aluminous solutions. When aluminous substances are heated by the blowpipe with nitrate of cobalt, they acquire a blue colour, which is only distinctly seen after the mixture has cooled, and by daylight.

§ XLIII. SILICIUM.

FROM experiments upon the action of potassium upon *silica*, Sir H. Davy concluded that that earth consisted of a peculiar inflammable basis, combined with its weight of oxygen, and he called the basis *Silicium*. This estimate of the composition of silica was deduced from the quantity of potassium required for its decomposition; the subject has since received further elucidation, and the correctness of the above statement has, to a great extent, been confirmed.

In the year 1824, silicium was obtained in its pure state by Berzelius, and from its properties, presently to be described, he has placed it, correctly, perhaps, among the simple non-metallic combustibles; indeed, it bears a strong resemblance to boron. Before, however, we remove it from the class of bodies with which it has usually been associated, it

may be well to wait till its general characters have been more satisfactorily studied. From the ample account of this substance, given by Berzelius, the following details are chiefly extracted.

He recommends, as the best source of silicium, the *silico-fluoride of potassium*, which is prepared by passing silico-fluoric acid into a solution of potassa, evaporating to dryness, and heating the residue nearly, but not quite, to redness. The salt thus obtained is to be well mixed with eight or nine-tenths of its weight of potassium, and the mixture introduced into a green glass tube and heated: before it acquires a red heat, its contents become ignited, in consequence of the chemical action that ensues, and the potassium is burned at the expense of the silica; a brown mass is thus obtained, consisting of fluoride of potassium, siliciuret of potassium, and a portion of the undecomposed salt: this is thrown into cold water, which occasions the evolution of hydrogen, resulting from the action of the siliciuret, the potassium of which is converted into potassa, and the silicium set free. When the effervescence is over, and the fluid has become clear, it is poured off from the residue, which is again washed, allowed to subside, and separated by decantation as before. These first washings must be performed with cold water, otherwise the alkali re-acts on the silicium, which, however, may now be thoroughly edulcorated with boiling water. It remains in the form of a dark-brown powder, infusible, and a non-conductor of electricity. Its properties are remarkably different before and after the application of a red heat: *before it has been heated* it burns easily in the air; but the superficial formation of silica prevents its entire combustion: in oxygen it burns brilliantly, and however carefully prepared, it always produces a little moisture. It is not acted upon either by sulphuric, nitric, or nitrohydrochloric acids, even when aided by heat. Liquid hydrofluoric acid readily dissolves it, evolving hydrogen: it is also dissolved when heated in a solution of caustic potassa. Silicium, *after it has been heated*, (obtained, for instance, by washing that which has been partially burned in the air, with hydrofluoric acid, to remove the superficial silica,) sinks in sulphuric acid, is incombustible before the blowpipe and in oxygen, and is not acted on by hydrofluoric acid, nor by caustic potassa; but it is easily dissolved in a mixture of hydrofluoric and nitric acids.

Silicium may be perfectly oxidized, and entirely converted into *silica* or *silicic acid*, by mixing it with dry carbonate of potassa, and heating to redness; it burns at the expense of the oxygen of the carbonic acid, and a *silicate of potassa* is obtained. Fused nitrate of potassa has no action upon it; but the addition of a little dry carbonate of potassa causes immediate deflagration: this paradoxical appearance depends upon the circumstance that the attraction of silicium for oxygen is influenced by the presence of the alkali, which has a high attraction for silica; just as the effect of zinc upon water is influenced by the presence of an acid, having an attraction for the oxide of zinc about to be produced. Carbonic acid is so weak that it does not prevent the action of the alkali: and as silicium has a stronger attraction for oxygen than carbon, it is oxidized at the expense of the carbonic acid. Nitric acid, on the other hand, is a strong acid, which entirely prevents this action of the alkali in the saltpetre upon the silicium; and silicium, at the temperature at which

saltpetre fuses, does not become oxidized; but if the heat be raised to whiteness, the silicium is then speedily oxidized by the decomposition of the nitric acid, and intense combustion ensues. Heated with the hydrated caustic alkalis, silicium burns in the oxygen of the water which they contain.

The equivalent of silicium has been variously estimated; according to Berzelius, silica is composed of 51.6 oxygen, and 48.4 silicium, and regarding it as a *protoxide*, this would give 7.5 as the equivalent of silicium, for $51.6 : 48.4 :: 8 : 7.5$. But Berzelius considers silica as a compound of 1 atom of base + 3 oxygen, hence 22.5 is his equivalent of silicium, and silica would be represented by $(Si + 3 O)$, or $22.5 + 24 = 46.5$. Others regard silica as a *protoxide*, and as composed of equal weights of base and oxygen, so that the equivalent of silicium will be identical with that of oxygen, or 8, an estimate closely consistent with the few analytical proofs which we have, and conveniently applicable to the siliceous compounds.

OXIDE OF SILICIUM, SILICA, OR SILICIC ACID, $(Si + O)$, Si , or Si' .—This, which is the only known combination of silicium with oxygen, is a very abundant natural product; it exists pure in some varieties of *rock-crystal*, and nearly pure in *flint**. It may be obtained by heating colourless rock-crystal to redness, quenching it in water, and reducing it to a

* The following are the principal minerals containing silica pure or nearly so.

i. *Rock-crystal* or *Quartz*, which may be considered as pure silica. It crystallizes in the form of a six-sided prism, ended by six-sided pyramids; some varieties are perfectly transparent and colourless; others white and more or less opaque. Its specific gravity is 2.6. It is so hard as to give sparks when struck with steel, and is nearly infusible. The primitive crystal, which is very rare, is an obtuse rhomboid, the angles of which are $94^{\circ} 24'$, and $85^{\circ} 36'$. The finest specimens are brought from Madagascar and the Alps. The perfectly transparent crystals found near Bristol, and in Cornwall, are sometimes called *Bristol* and *Cornish diamonds*. The fine crystals are cut into ornaments, and sometimes used as a substitute for glass in spectacles; they are then termed *pebbles*, and do not so readily become scratched as glass.

Brown and yellow crystals of quartz are found in great beauty in the mountain of Cairn Gorm, in Scotland, and are much admired for seal-stones, &c.: they are sometimes improperly termed *topazes*.

Purple quartz or *amethyst*, is tinged with a little iron and manganese. *Rose*

quartz derives [its colour from manganese. *Prase* or *green quartz*, contains actinolite; and *chrysoprase* is tinged of a delicate apple-green by oxide of nickel. *Avanturine* is a beautiful variety of quartz, of a rich brown colour, which, from a peculiarity of texture, appears filled with bright spangles; the finest specimens are from Spain: it is often imitated. Small crystals of quartz, tinged with iron, are found in Spain, and have been termed *hyacinths of Compostella*.

ii. *Flint*, *Chalcedony*, *Carnelian*, *Onyx*, *Sardonyx*, and *Bloodstone* or *Heliotrope*, and the numerous varieties of *Agates*, are principally composed of quartz, with various tinging materials.

iii. *Opal* is among the most beautiful productions of the mineral world; it is a compound of about 90 silica and 10 water, and is distinguished by its very brilliant play of colours. The finest specimens come exclusively from Hungary. There is a variety of opal called *hydropbane*, which is white and opaque till immersed in water; it then resembles the former.

Common opal is usually of a dirty white, and does not exhibit the colours of the noble opal; it contains silica and water, with a little oxide of iron, and is not of unfrequent occurrence. The

fine powder; in this state it is silica almost perfectly pure. Fuse 1 part of this powder with 8 or 10 of carbonate of soda, in a silver or platinum crucible. Dissolve the mass formed in water, add slight excess of hydrochloric acid, and evaporate to dryness. Wash the dry mass in boiling distilled water upon a filter, and the white substance which remains is silica. This is the usual process; but the earth obtained by simply reducing the colourless rock-crystal to powder is very pure, though it sometimes contains traces of oxide of iron and manganese, and of alumina. A very pure silica may be obtained, by the fusion of fine white sand, or powdered rock-crystal, with carbonate of lime: the resulting compound of lime and silica may be decomposed by dilute hydrochloric acid; and the silica, after having been duly washed, is in the form of a very light powder. When silico-fluoric gas is passed into water, the silica which is precipitated, after having been washed and dried, is also very pure, and in a state of extreme mechanical division.

Silica, in its ordinary state, is a harsh white powder, insoluble in water and in most other solvents, and infusible except in the intense heat of the flame of a spirit-lamp, urged by the oxygen blowpipe: it then melts with difficulty into a colourless globule. Its specific gravity is 2.66.

When recently precipitated, and in the state of *hydrate*, it is to a certain extent soluble in water and in the acids. The aqueous solution is tasteless, and, when evaporated, deposits gelatinous silica, which, on being dried, becomes again quite insoluble: the acid solutions also exhibit no indication of saline combination, but when evaporated leave pure silica. Silica is often found in spring and mineral waters; and in the fountains of Reikum and the boiling geysers of Iceland it is contained in such quantities as to be deposited by them in the form of a porous incrustation. According to the view of the atomic constitution of silica above suggested, it will consist of

					Berzelius.	
Silicium	1	.	.	8	.	50 . . . 48.4
Oxygen	1	.	.	8	.	50 . . . 51.6
<hr/>						
Silica	1			16		100 . . . 100.0

CHLORIDE OF SILICIUM. (*Si + Cl.*)—Silicium burns, when heated in chlorine, or when a current of chlorine is passed over red-hot silicium in a porcelain tube, and a fuming liquid is the result, of a yellow colour, extremely volatile, and irritating to the nose and eyes, and which, exposed to moist air, forms hydrochloric acid and silica. Dropped into water it floats upon that fluid, and is then dissolved, depositing a little gelatinous silica: hydrochloric acid is also formed. When potassium is heated in its vapour, it burns with the production of siliciuret and chloride of potassium. (BERZELIUS.) Chloride of silicium may also be obtained by passing dry chlorine over an intimate mixture of silica and

substance called *menilite* from Menil Montant, near Paris, is nearly allied to common opal. It is found in irregular masses in a bed of clay.

iv. *Pitchstone*, so called from its resinous appearance, contains 73 per

cent. of silica. *Obsidian*, a volcanic product, contains 78 per cent. of silica, and much resembles glass in appearance; and the different kinds of *pumice* are nearly of similar composition.

finely-divided charcoal in a red-hot porcelain tube: the chloride may be condensed in a properly-cooled receiver; as it generally contains excess of chlorine it may be agitated with a little dry mercury and redistilled. (OERSTED.)

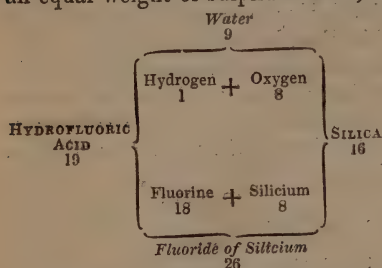
					Berzelius.	
Silicium	1	8	18.3	17.3		
Chlorine	1	36	81.7	82.7		
<hr/>						
Chloride of silicium	1	44	100.0	100.0		

IODIDE OF SILICIUM has not been formed.

BROMIDE OF SILICIUM (*si + b*) was obtained by Serullas by passing the vapour of bromine over heated silicium: it is a colourless fuming liquid, heavier than sulphuric acid. It congeals at 10° and boils at 300° . It is decomposed when gently heated with potassium, with explosive violence; water converts it into hydrobromic acid and silica. (*Phil. Mag. and Ann.*, xi. 395.)

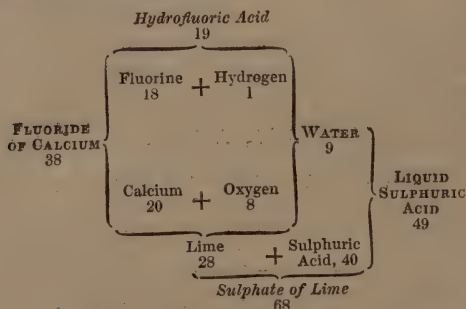
FLUORIDE OF SILICIUM.—The only acid body which acts energetically upon silica is the hydrofluoric acid. The result of this action is a gaseous compound, which has been called *silicated fluoric acid*, or *fluosilicic acid*; it is probably a binary compound of silicium and fluorine.

To obtain this gaseous compound, 3 parts of fluor spar and 2 of powdered glass, or of silica finely powdered, are mixed in a retort with about an equal weight of sulphuric acid; the gas evolved is to be collected over



mercury, and when its production slackens, it may be accelerated by a gentle heat. The mercury and the glass vessels employed must be quite dry. This decomposition depends upon the evolution of hydrofluoric acid and its action upon the silica, water and fluoride of silicium being the ultimate results, as in the annexed diagram.

The hydrofluoric acid is derived as follows, from the action of hydrated sulphuric acid on fluoride of calcium.



Silicated fluoric acid is a colourless gas; its odour is acrid, somewhat resembling hydrochloric acid; its taste very sour; its specific gravity is 3.6 compared with air: 100 cubic inches weigh about 112 grains. It

extinguishes the flame of a taper. It produces white fumes when in contact with damp air, and when exposed to water it is absorbed, and a soluble compound of silica with hydrofluoric acid is formed, whilst a quantity of silica is at the same time precipitated. If the beak of the retort from which the gas is issuing be plunged into a basin of water, it is soon choked by the copious deposit of hydrated silica, which sometimes forms tubes through the water, by which the gas escapes directly into the air. When it is intended to saturate water with the gas (it takes up about 260 volumes), this effect may be prevented by agitation, or better by suffering the gas to escape through a stratum of mercury into water above it.

Water thus saturated becomes a gelatinous mass, from which the acid liquor may be separated, by placing it, without pressure, upon a linen filter. The liquor is sour, and, when saturated with the fixed alkalis, becomes gelatinous, but not turbid: with barytic salts it soon deposits a white precipitate. Saturated with potassa, and evaporated to dryness, it yields the *silico-fluoride of potassium*, already adverted to as a source of silicium. It is a hydrofluat of fluoride of silicium, and when evaporated, gaseous fluoride of silicium escapes, and hydrofluoric acid is evolved, so that, although the original aqueous solution does not act upon glass, it immediately does so when so far concentrated by evaporation as to generate the free hydrofluoric acid.

When 1 volume of silicated fluoric acid is mixed with 2 of ammonia, a total condensation ensues, and a dry *silico-fluat of ammonia* results, which is decomposed by the action of water. When silico-fluoric gas is passed into liquid ammonia, the whole of the silicium is separated in the form of silica, and hydrofluat of ammonia remains in solution. Potassium heated in this gas, burns, and produces silico-fluoride of potassium.

Fluoride of silicium consists of

				J. Davy.	Berzelius:
Silicium	1	8	30.8	30.7	29.32
Fluorine	1	18	69.2	69.3	71.68
Fluoride of silicium	1	26	100.0	100.0	100.00

SILICO-FLUORIDE OF POTASSIUM. ($po + 2si + 3f$).—When this salt is formed by passing silicated fluoric acid into a solution of potassa, it falls in the form of an iridescent jelly, which dries into a white powder, very sparingly soluble in boiling water, and yielding minute anhydrous crystals. It appears that in the formation of this salt the potassa acting on the hydrofluoric acid forms fluoride of potassium, which combines with the fluoride of silicium, in the proportion of 1 equivalent of the former to 2 of the latter; or that silico-fluoride of potassium consists of

Potassium	1	40	36.4
Silicium	2	16	14.5
Fluorine	3	54	49.1
Silico-fluoride of potassium	1	110	100.0

SILICO-FLUORIDE OF SODIUM is obtained in the same way as the potassium salt, but falls more readily, and is not iridescent: it is more soluble, especially in hot water. It may be obtained in small shining crystals, which are anhydrous hexangular prisms.

SILICO-FLUORIDE OF BARIUM is gradually precipitated when silico-fluoric acid is mixed with chloride of barium, in anhydrous microscopic crystals, of difficult solubility in water.

The *silico-fluorides of strontium, calcium, magnesium, and lead*, are formed by dissolving their carbonates in silico-fluoric acid. The salts of magnesium and of lead are very soluble. The *silico-fluorides of manganese, iron, zinc, cobalt, nickel, and copper*, are soluble in water, and crystallize in similar hexagonal prisms, probably isomorphous, which contain respectively 1 equivalent of the silico-fluoride, and 7 equivalents of water of crystallization.

SULPHURET OF SILICIUM.—Silicium, when heated intensely, burns brilliantly in the vapour of sulphur, and a white earthy compound is the result, which is not affected by dry air, and when heated to redness is slowly decomposed, with the production of sulphurous acid. It is rapidly decomposed by water; in moist air it exhales sulphuretted hydrogen, and that gas is abundantly evolved by its action on water, whilst the silica is retained in aqueous solution, and no sulphur is deposited: hence it consists of

				Berzelius.	
Silicium	1	8	33.3
Sulphur	1	16	66.7
<hr/>				<hr/>	
Sulphuret of silicium		1		24	100.0
					100

PHOSPHURET OF SILICIUM has not been formed.

CARBURET OF SILICIUM.—When the potassium employed in the reduction of silica contains carbon, the resulting silicium is partly in the state of *carburet*: it has a dark colour, and gives off carbonic acid when burned.

ALLOYS OF SILICIUM.—Berzelius remarks that silicium only combines with the metals when in its nascent state, and that when once insulated no such compounds can be formed. When silica is reduced in contact of platinum, it becomes penetrated by silicium; but silicium may afterwards be heated white-hot in a platinum crucible without any such effect.

SILICATES.—It is obvious from the preceding statement, that there are no salts, properly so termed, in which the oxy-acids are combined with silica, but that silicium forms haloid compounds. But silica readily combines in the manner of an oxide or acid, with many of the salifiable bases; hence the term *silicic acid* applied to it, and *silicates* to its compounds. Of these compounds several are most importantly useful, and many of them are found as natural products, forming crystallized minerals, and parts of the strata or rocks that constitute the exterior crust of the globe. Glass, pottery, and porcelain, in all their varieties, are combinations of silica, and it is an essential ingredient in soils. I shall first describe some of the best defined silicates, and then advert to the manufacture of glass, and of the different kinds of porcelain and pottery, in which it is concerned.

SILICATE OF POTASSA.—When 1 part of silica and 4 of caustic potassa are fused together, and slowly cooled, a part of the compound may be poured out of the crucible before the whole has solidified, and pearly crystals are formed in the residuary portion, which are apparently composed of 1 atom of silica and 1 of potassa. (BERZELIUS.) When 1 part of silica and 2·5 of carbonate of potassa are fused together, the carbonic acid is expelled, and a *bisilicate of potassa* is the result. (H. ROSE.) These silicates are soluble in water, forming the *liquor silicum* of the older chemists. This solution may also be obtained by digesting gelatinous hydrate of silica, or very finely-divided silica in solution of potassa; the silica is thrown down from these solutions in the gelatinous state, by the acids. When potassa and great excess of silica are fused together, a species of *glass* is the result, which however is still acted upon by water; this solubility is greatly impaired by the presence of lime and alumina. The atomic composition of the different vitreous compounds that may be thus formed, cannot be ascertained, but they generally contain from 15 to 20 equivalents of silica to 1 of potassa. When 15 parts of silica, 10 of carbonate of potassa, and 1 of powdered charcoal, are fused together for about six hours, a vitreous compound is obtained, which when dissolved by boiling in water, filtered, and concentrated by evaporation, may be used to render wood, paper-hangings, scenery, and other such articles, incombustible: it may be mixed with alumina or chalk, and applied in the manner of a paint. (FUCHS, *Schweigger's Journal*, xxiv. 378.)

SILICATE OF SODA.—The compounds of silica and soda are analogous to the preceding, but as carbonate of soda is not deliquescent, some of the soluble vitreous compounds which it forms effloresce on exposure, instead of running into a liquid, or remaining moist upon the surface. A solution of silica in soda has been employed as an addition to soap; it is said to improve its detergent powers. Silicate of soda always has a greenish or bluish tint, however pure the materials used in its production, and this is an obstacle to the substitution of soda for potassa in certain kinds of glass.

SILICATE OF LIME.—Silica and lime may be combined by fusion, but the results of their mutual action have not been minutely examined. Under the article GLASS, in AIKIN'S *Dictionary*, some valuable facts will be found in reference to these combinations. There are some minerals, and among them *table-spar* or *Wollastonite* (composed of 50 silica, 45 lime), which are silicates of lime. *Apophyllite* is a *hydrated silicate of lime and potassa*, composed of 1 atom of tersilicate of potassa, 8 of tersilicate of lime, and 16 water ($P + 3Si' + 8(C + 3Si') + 16q$).

SILICATE OF BARYTA.—2 parts of silica and 1 of baryta fuse together into a porous slag. A similar combination may be obtained with *strontia*.

SILICATE OF MAGNESIA.—Several minerals appear to be definite compounds of silica and magnesia. *Olivin*, or *chrysolite*, is a simple silicate or magnesia ($M + Si'$) with variable proportions of oxide of iron. *Steatite* is a tersilicate of magnesia ($M + 3Si'$), and *meerschaum* a hydrated bisi-

licate. According to Morveau, silica and magnesia may be combined by fusion at a white heat.

SILICATE OF LIME AND MAGNESIA.—*Pyroxene*, or *augite*, is a crystallized mineral, composed of 1 atom of bisilicate of lime, and 1 of bisilicate of magnesia. Sometimes oxide of iron replaces part of the magnesia. Similar crystals are occasionally found in the slags of iron-furnaces, and may also be formed artificially. (MITSCHERLICH and BERTHIER, *Ann. de Ch. et Ph.*, xxiv. 355.) Equal parts of lime, magnesia, and silica, may be fused into a green glass, which strikes fire with steel. (ACHARD.) *Amphibol*, or *hornblende*, may be regarded as a compound of 1 atom of tersilicate of lime, and 3 of bisilicate of magnesia (with oxides of iron and manganese).

SILICATE OF MANGANESE.—This compound occurs native in Dalecarlia. The red siliceous manganese is a bisilicate of the protoxide of manganese ($\text{MAN} + 2 \text{Si}'$).

SILICATE OF IRON.—A silicate and bisilicate of protoxide of iron is found in the slag from the smelting of the ferro-sulphurets of copper. Davy found the ochraceous sediment of the chalybeate springs of Lucca to consist of *silicate of peroxide of iron*, the water probably holding a protosilicate in solution. There are several other minerals which are silicates, or hydrated silicates of iron.

SILICATE OF ZINC occurs native under the name of *electric calamine*: it crystallizes in rhombic prisms, composed of 2 atoms of silicate of oxide of zinc, and 1 of water.

SILICATE OF COPPER is thrown down upon the mixture of sulphate or nitrate of copper with silicate of potassa. It occurs native in *diopase*, or *copper-emerald*, which is apparently composed of 2 atoms of oxide of copper, 3 of silica, and 2 of water.

SILICATE OF LEAD.—This compound exists in flint-glass, and is often used as a glaze for porcelain or earthenware, hence the poisonous quality conferred upon certain articles of food, when kept in earthen vessels thus glazed. A silicate of lead is easily formed (of variable composition) by fusing silica with oxide of lead; a yellow glass is the result. Some of the Chinese figures (often said to be made of rice) are a glass composed of 41 oxide of lead, 39 silica, 7 alumina. (KLAPROTH.)

SILICATE OF ALUMINA.—The different kinds of *clay* are probably mixtures, rather than compounds, of silica, alumina, and water. The best clays for the purposes of pottery consist of about 3 proportionals of silica and 1 of alumina; or by weight 48 and 18. The following are the principal varieties used here. 1. *Porcelain Clay*, derived principally from the decomposition of felspar, and containing silica and alumina, sometimes with traces of oxide of iron; it is very difficult of fusion. 2. *Marly Clay*, which, with silica and alumina, contains a portion of carbonate of lime; it is much used in making pale bricks, and as a manure; and when highly heated enters into fusion. 3. *Pipe Clay*, which is very plastic and tenacious, and requires a higher temperature than the preceding for fusion; when burned it is of a cream-colour, and used for tobacco-pipes and white

pottery. 4. *Potters' Clay* is of a reddish or gray colour, and becomes red when heated; it fuses at a bright red-heat: mixed with sand it is manufactured into red bricks, and tiles, and is also used for coarse pottery.

The mineral called *Cyanite* (Disthene), which is not uncommon in primitive rocks, is a *disilicate of alumina* ($2\text{Al} + \text{Si}$). *Andalusite* is also a silicate of alumina. There are also many ternary and quaternary silicates in the mineral kingdom, a few of which I shall here enumerate, selected chiefly from the account of them given by L. Gmelin*. *Topaz* = 2 silicate of alumina + 1 fluoride of aluminum. *Felspar* = 1 tersilicate of potassa + 3 tersilicate of alumina. *Leucite* = 1 bisilicate of potassa + 3 bisilicate of alumina. *Mica*, a silicate of alumina with tersilicate of potassa. *Pinit* = 1 tersilicate of potassa + 6 silicate of alumina (and oxide of iron). *Albite* = 1 tersilicate of soda + 3 tersilicate of alumina. *Sodalite* = 1 chloride of sodium + 2 silicate of soda + 6 silicate of alumina. *Nephelin* = 1 silicate of potassa + 2 silicate of soda + 12 silicate of alumina. *Analcime* = 1 bisilicate of soda + 3 bisilicate of alumina + 2 water. *Natrolite* = 1 tersilicate of soda + 3 silicate of alumina + 2 water. *Petalite* = 1 tersilicate of lithia + 3 tersilicate of alumina. *Spodumene* = 1 bisilicate of lithia + 4 bisilicate of alumina. *Barytic Harmotome* = 1 quatersilicate of baryta + 4 bisilicate of alumina + 6 water. *Azinite* = 1 bisilicate of lime + 3 silicate of alumina (with oxide of iron, manganese, and boracic acid?). *Prehnite* = 1 silicate of lime + 3 silicate of alumina. *Stilbite* = 1 tersilicate of lime + 3 tersilicate of alumina + 6 water. *Chabasite* = 1 bisilicate of lime + 3 bisilicate of alumina + 6 water. *Laumonite* = 1 bisilicate of lime + 3 bisilicate of alumina + 4 water. *Emerald* = 1 tersilicate of glucina + 2 tersilicate of alumina. *Euclase* = 1 silicate of glucina + 2 silicate of alumina. *Zircon* = silicate of zirconia, or 1 silica + 1 zirconia. *Sphene* = 1 tersilicate of lime + 1 sesquitanite of lime.

POTTERY AND PORCELAIN.—The better kind of *pottery*, called in this country *Staffordshire ware*, is made of an artificial mixture of alumina and silica; the former obtained in the form of a fine clay, from Devonshire chiefly; and the latter, consisting of chert or flint, which is heated red-hot, quenched in water, and then reduced to powder. Each material, carefully powdered and sifted, is diffused through water, mixed by measure, and brought to a due consistency by evaporation: it is then highly plastic, and formed upon the potter's wheel and lathe into various circular vessels, or moulded into other forms, which, after having been dried in a warm room, are enclosed in baked clay cases resembling handboxes, and called *seggars*; these are ranged in the kiln so as nearly to fill it, leaving only space enough for the fuel; here the ware is kept red-hot for a considerable time, and thus brought to the state of *biscuit*. This is afterwards *glazed*, which is done “by dipping the biscuit-ware into a tub containing a mixture of about 60 parts of litharge, 10 of clay, and 20 of ground flint, diffused in water to a creamy consistence, and when taken

* The numbers imply atoms or equivalents, according with those above given. It is obvious that very different views of the atomic constitution of minerals may

be taken, from those given in the text: and as yet we have no experiments to guide us in our decisions on this point.

out, enough adheres to the piece to give an uniform glazing when again heated. The pieces are then again packed up in the seggars, with small bits of pottery interposed between each, and fired in a kiln as before. The glazing-mixture fuses at a very moderate heat, and gives an uniform glossy coating, which finishes the process when it is intended for common white ware." (AIKIN'S Dictionary. Art. POTTERY.)

The patterns upon ordinary porcelain, which are chiefly in blue, in consequence of the facility of applying cobalt, are generally first printed off upon paper, which is applied to the plate or other article while in the state of biscuit; the colour adheres permanently to the surface when heat is properly applied.

The manufacture of *porcelain* is a most refined branch of art; the materials are selected with the greatest caution, it being necessary that the compound should remain perfectly white after exposure to heat: it is also required that it should endure a very high temperature without fusing, and at the same time acquire a semivitreous texture and a peculiar degree of translucency and toughness. These qualities are united in some of the Oriental porcelain, or *China*, and in some of the old Dresden, but they are rarely found co-existent in that of modern European manufacture. Some of the French and English porcelain, especially that made at Sèvres and at Worcester, is extremely white, and duly translucent, but it is more apt to crack by sudden changes of temperature; more brittle, and consequently requires to be formed into thicker and heavier vessels; and more fusible than the finest porcelains of Japan and China.

The colours employed in painting porcelain are the same metallic oxides used for colouring glass, and in all the more delicate patterns they are laid on with a camel-hair pencil, and generally previously mixed with a little oil of spike-lavender or of turpentine. Where several colours are used, they often require various temperatures for their perfection; in which case those that bear the highest heat are first applied, and subsequently those which are brought out at lower temperatures. This art of painting on porcelain or in enamel is of the most delicate description; much experience and skill are required in it, and with every care there are frequent failures; hence it is attended with considerable expense. The gilding of porcelain is generally performed by applying finely-divided gold mixed up with gum-water and borax; upon the application of heat the gum burns off, and the borax vitrifying upon the surface causes the gold firmly to adhere; it is afterwards burnished.

CRUCIBLES.—In the manufacture of various kinds of pottery employed in the chemical laboratory, and especially in regard to *crucibles*, many difficulties occur; and many requisites are necessary, which cannot be united in the same vessel: to the late Mr. Wedgwood we are indebted for vast improvements in this as well as in other branches of the art. Crucibles composed of one part of pure clay mixed with about three parts of coarse and pure sand, slowly dried and annealed, resist a very high temperature without fusion, and generally retain metallic substances; but where the metals are suffered to oxidize, there are few which do not act upon any earthen vessel, and some cause its rapid fusion, as the oxides of lead, bismuth, &c. Where saline fluxes are used, the best crucibles

will always suffer, but platinum may often be employed in these cases, and the chemist is thus enabled to combat many difficulties which were nearly insurmountable before that metal was thus applied. Whenever siliceous and aluminous earths are blended, as in the mixture of clay and sand, the compound softens, and the vessel loses its shape when exposed to a long-continued white heat, and this is the case with the *Hessian* crucibles: the most refractory of all vessels are those made entirely of clay, coarsely-powdered burned clay being used as a substitute for the sand. Such a compound resists the action of saline fluxes longer than any other, and is therefore used for the pots in glass-furnaces. A *Hessian* crucible lined with purer clay is rendered much more retentive; and a thin china cup, or other dense porcelain, resists the action of saline matters in fusion for a considerable time. Plumbago is a very good material for crucibles, and applicable to many purposes; when mixed with clay it forms a very difficultly-fusible compound, and is protected from the action of the air at high temperatures; it is well calculated for small table-furnaces. Wrought-iron, and the best cast-iron crucibles, are used for the fusion of several metallic substances which melt at a bright red-heat. The latter are used in the Mint for the fusion of silver; the gold is melted in black-lead or plumbago pots.

LUTES.—Under the term *Lutes* a variety of compounds are used by the practical chemist for the purpose of securing the junctures of vessels or protecting them from the action of heat. Slips of wetted bladder, linseed meal made into a paste with gum-water, white of egg and quick-lime, glazier's putty, which consists of chalk and linseed oil, and *fat lute*, composed of pipe-clay and drying oil, well beaten to a stiff mass, are very useful lutes for retaining fumes and vapours and joining vessels to each other, but earthy compounds are required to withstand the action of a high temperature. Windsor loam, or an artificial mixture of clay and sand well beaten into a stiff paste, and then thinned with water and applied by a brush in successive layers, to retorts, tubes, gun-barrels, &c., enables them to bear a very high temperature; if a thick coating is required, great care should be taken that the cracks are filled up as it dries, and often a little tow mixed up with the lute renders it more permanent and applicable. If the lute is intended to vitrify, as, for instance, to prevent the porosity of earthenware at high temperatures, a portion of borax or of red-lead may be mixed up with it. Respecting the selection and management of crucibles, lutes, &c., the reader is referred to Mr. Faraday's *Manipulation*.

MORTARS AND CEMENTS.—*Mortar*, or the cement used in building, is a compound of several earthy substances, one of which is always lime; for much valuable information relating to this important subject we are indebted to the late Mr. Smeaton, (*History of the Eddystone Lighthouse*), and an excellent summary of the principal facts connected with it will be found in *AIKIN'S Dictionary*. (Art. CEMENTS.) The ordinary mode of making mortar consists in mixing a quantity of common sand with slaked lime, without any careful attention to the quantity or purity of the materials; but it has been shown by Mr. Smeaton, that the presence of unburnt clay prevents the induration of the mortar, and the sand used in London always contains it; the lime too is often imperfectly burned and seldom

duly selected; that which contains a portion of alumina and oxide of iron being preferable to the purer varieties: hence the advantage of *Dorking lime*, or *meagre lime*, as it is usually called. The sand should be sharp and large grained, and perfectly free from salt, which always prevents the mixture from becoming hard. The addition of calcined ferruginous clay, or calcined basalt, or black oxide of iron, gives mortar the property of becoming hard under water.

The mutual action which the substances constituting the different kinds of mortar undergo, has hitherto been but imperfectly examined by the chemist; to M. Vicat we are indebted for a curious and important series of experiments upon this subject, and his work may be consulted with much advantage, by those who are concerned in investigations of this nature. (*Recherches Expérimentales sur les Chaux de Construction, les Bétons, et les Mortiers ordinaires.* Paris, 1818.)

MANUFACTURE OF GLASS.—Of this important and extensive subject I have only room for a very brief outline: for details I must refer to the authorities quoted, to the volume of LARDNER'S *Cyclopædia*, which treats upon the manufacture of glass and pottery, and to DUMAS, *Chim. appl. aux Arts*.

GLASS is essentially a compound of silica with potassa or soda, a variety of other substances being occasionally added for particular purposes, among which oxide of lead is perhaps the most important. The silica used in the manufacture of glass, is of various degrees of purity; fine white sand is generally employed in this country; flints, and the white quartz pebbles, abundant in some rivers, are also occasionally used. The alkali is either potassa or soda; purified soda or pearlash being preferred for fine glass; while less pure alkalis, such as wood-ash, barilla, and kelp, are used for common glass, where the impurities contained in those substances are of no importance. The alkali is always used in the state of carbonate, but it loses its carbonic acid during combination with the silica; the quantity employed is about half the weight of the silica, but there is some loss during the process, by evaporation*.

A glass composed solely of silica and alkali requires a very high temperature for its perfect fusion, and is very difficult to work, so that various substances are added, with the intention of forming a more fusible, colourless, dense, and transparent compound: *oxide of lead*, in the form of litharge or minium, is very efficacious in this respect: it increases the

* All common glass when reduced to a fine powder is more or less acted on by boiling water, which separates the alkali, and its entire disintegration seems only to be prevented by the insolubility of the silica. Indeed, if finely-powdered flint-glass be placed upon turmeric-paper and merely moistened, it powerfully reddens the test. Glass which has long been exposed to the weather frequently exhibits a beautiful iridescent appearance, and is so far decayed that it may be scratched with the nail: several years ago I examined some bottles of wine

which had lain in a wet cellar near the Bank, upwards of 150 years, having been deposited there (as circumstances proved) previous to the great fire of London in 1666. The glass was soft and greatly corroded upon the surface, in consequence of the abstraction of its alkali. The wine appeared to have been Malaga and Claret: the latter had perished, but the former was still vinous. See *Quart. Journ.*, xx. 262, where there is a paper on the solubility of glass by Mr. T. Griffiths.

fusibility of the compound, gives it greater tenaciousness when red-hot, increases its refractive power, and enables it to bear sudden changes of temperature. It is a copious ingredient in the *London flint-glass*, celebrated for its brilliancy when cut, and used for most optical purposes. But lead, though it confers these advantages, is productive of some evil; it renders the glass so soft as easily to scratch, and so fusible that it softens at a dull red-heat, a quality which, though sometimes desirable, is often disadvantageous in its chemical applications. It is also very difficult to obtain a mass of glass containing lead, of equal density throughout; it is generally wavy, a defect especially felt in selecting glass for optical purposes.

Boracic acid and borax form an admirable flux for glass-making, but the expense of those materials confines them almost entirely to the manufacture of artificial gems, or of glass applicable to particular purposes only.

Black oxide of manganese has long been used in glass-making; it was formerly called *glass-soap*, a term implying its power of cleansing certain impurities, and especially the green tinge which is apt to arise from impure alkali; but if it be added at all in excess, it communicates a purple tinge, more or less intense according to its quantity. This purple hue is destroyed by charcoal, or by thrusting a billet of wood into the glass-pot, which causes a slight effervescence, and the colour disappears. There can be little doubt that the carbon acts by deoxidizing the manganese, for if a little nitre be added, the purple colour returns. Lime in very small quantities, (8 or 10 parts of chalk to 100 of silica,) is sometimes added to glass: it acts as a flux, but it endangers the transparency of the compound.

White arsenic is also used as a very cheap and powerful flux; and nitre, in small quantities, is employed to destroy any impurities arising from carbonaceous matter.

The materials for the manufacture of glass are sometimes submitted to an operation called *fritting*, before they are transferred to the regular glass-furnace. It consists in exposing them to a dull red-heat, by which moisture and carbonic acid are expelled, and a slight degree of chemical action induced; this also prevents the excessive swelling up of the materials in the glass-pots, and renders the process of vitrification more certain and expeditious. The term *frit*, however, is now generally applied to the mere mixture of materials, which, without previous preparation, are at once melted in the furnace.

The glass-pots are placed round a dome-shaped furnace, built upon arches, and open beneath for the free admission of air; there are generally six in each furnace, and they are entirely enclosed except at an orifice on the side, opening into a small recess formed by the alternate projections of the masonry and the flues, in which recess the workmen stand. Coal is the fuel employed, and the furnace is so built that a rapid current of flame may be directed round each glass-pot, which afterwards passes out with the smoke into the dome and chimney, heating a broad covered shelf in its passage, which is sometimes used as an annealing-oven.

In the construction of the furnace and pots, the greatest care is required; especially in the latter, which have not only to resist long-

continued heat, but also, as far as possible, the action of ingredients which tend to accelerate their fusion or vitrification. They are usually made entirely of a refractory clay, one portion being crude or unburnt, and another calcined and powdered; the latter being the remains of former furnaces when pulled down for repairs.

The frit is introduced into the glass-pots through the side opening above-mentioned, and being heated to bright redness, becomes of a pasty consistency, and at length perfectly fuses. A quantity of impurities subside to the bottom of the pot, and partly rise to its surface. The scum, known under the name of *sandever**, consists chiefly of saline substances, partly volatile at the high temperature of the furnace, which are removed from time to time, and sold to metal refiners as a powerful flux. The sandever, or *glass-gall*, being separated, the materials gradually become clearer, abundance of air bubbles are extricated, and at length the glass appears uniform and complete; the fire round the individual pot is then damped till its contents acquire a consistency fit for working, the whole process requiring about 48 hours from the time the pots are filled. At the working-heat, which is a full red, the glass has a very peculiar tenacious consistency, and as it adheres but feebly to polished metal, it is easily wrought and managed with iron tools.

All glass articles require to be carefully *annealed*, that is, suffered to cool very slowly, otherwise they are remarkably brittle and apt to crack, and even fly into many pieces upon the slightest touch of any hard substance, as is well shown in the small drops of green glass suddenly cooled by dropping them into water, and called *Rupert's drops*; the instant their thin end is broken off, they crumble into a powder with a kind of explosion. This phenomenon, according to Mr. Aikin, "depends upon some permanent and strong inequality of pressure, for when they are heated so red as to be soft, and merely let cool of themselves, the property of bursting is lost, and the specific gravity of the drop increased." What are termed *Proofs*, or *Bologna phials*, are also made of unannealed glass, and fly to pieces when a piece of flint or other hard and angular substance is dropped into them.

When large masses of glass which have been long in fusion are suffered to cool slowly, they frequently exhibit very singular crystalline appearances; there are often detached globular formations, of a very peculiar radiated texture, and looking exactly like foreign substances imbedded in the glass; sometimes it is opaque and crystalline, bearing a strong resemblance to certain mineral products; in these cases crystallization seems to have influenced the affinity of the elements, and the consequent composition of the products. Mr. Watt's experiments upon the fusion of basalt may be consulted in reference to this curious subject. (*Phil. Trans.*)

The exact composition of the different kinds of glass is scarcely known; the following proportions of the materials are, however, given in Messrs. AIKINS' *Dictionary*, to which the reader is referred for a valuable article upon the subject of glass: it must, however, be recol-

* This substance is scarcely known in our present glass-houses, in consequence of the pains bestowed upon the purification of the materials employed.

lected, that the composition of the perfect glass can only be remotely anticipated from a knowledge of the substances employed in its formation, in consequence of the changes which they undergo, and the volatility of some of them, at the high temperature to which they are subjected *. The specific heat of glass as determined by Regnault is 0.19768; but the composition of the specimen which he used is not stated. (*Ann. de Ch. et Ph.*, lxxiii. 34.)

Flint-glass. Specific gravity about 3.2.

120 parts of fine clear white sand
40 " purified pearlash
35 " litharge
13 " nitre

A small quantity of black oxide of manganese.

Crown-glass, or best window-glass.

200 parts of soda
300 " fine sand
33 " lime
250 " ground fragments of glass†.

Green Bottle-glass.

100 parts of sand
30 " coarse kelp
160 " lixivated earth of wood ashes
30 " fresh wood-ash
80 " brick clay
100 " fragments of glass.

Plate-glass, invented by Abraham Thevart in 1688, was first manufactured in Paris. It may be composed of

300 lbs. fine sand
200 lbs. soda
30 lbs. lime
32 oz. manganese
3 oz. cobalt azure
300 lbs. fragments of good glass.

These materials are brought into perfect fusion, and poured upon a hot iron or copper-plate; the mass is then rolled out, annealed, and afterwards polished by grinding with sand, emery, and colcothar. The difficulty of producing a perfect plate without specks, bubbles, or waves, may easily be conceived, and this, with the risk of breakage, renders a large plate extremely expensive.

The art of colouring glass, and of making *artificial gems*, is of an old

* Mr. Faraday has communicated to the Royal Society a paper on the manufacture of glass for optical purposes, containing much curious and valuable information upon the subject generally, and which should be consulted by those who are concerned in that difficult branch of the art of glass-making. He successfully availed himself of the use of *borate of lead* as one of its components. I am indebted to him for the following analyses of different specimens of flint-glass. (*Phil. Trans.*, 1830.)

Silica	51.93	48.24	44.30
Oxide of lead	33.28	40.12	43.05
Potassa	13.77	10.60	11.75
Alumina	0.47	0.58	0.50
Oxides of iron and manganese }	0.27	0.08	0.12
	99.72	99.62	99.72

† In the manufacture of all common glass a proportion of broken glass is usually mixed up with the raw materials, and is technically known under the name of *Cullet*.

date, and effected by metallic oxides. The *paste* for artificial gems generally contains borax, and should be kept in fusion till perfectly clear. The following proportions are recommended by M. Douault-Wieland. (*Ann. de Ch. et Ph.*, xix. 57.)

	Grains.
Powdered rock-crystal	4056
Red lead	6300
Pure potassa	2154
Borax	276
White arsenic	12

M. Lançon gives the following as ingredients for a good paste:—

	Grains.
Litharge	100
White sand	75
White tartar or pot-ash	10

The metals employed as colouring-materials are:—1. Gold. The purple of Cassius imparts a fine ruby tint. 2. Silver. Oxide or phosphate of silver gives a yellow colour. 3. Iron. The oxides of iron produce blue, green, yellow, and brown, depending upon the state of oxidizement and quantity. 4. Copper. The oxides of copper give a rich green; they also produce a red when mixed with a small proportion of tartar, which tends partially to reduce the oxide. 5. Antimony imparts a rich yellow. 6. Manganese. The black oxide of this metal, in large quantities, forms a black glass; in smaller quantities, various shades of purple. 7. Cobalt, in the state of oxide, gives beautiful blues of various shades; and with the yellow of antimony or lead it produces green. 8. Chrome produces fine greens and reds, depending upon its state of oxidizement.

White Enamel is merely glass, rendered more or less milky or opaque by the addition of oxide of tin; it forms the basis of many of the coloured enamels, which are tinged with the metallic oxides. Directions for the preparation of several good *enamel-colours* are given by Mr. Wynn, in the *Transactions of the Society of Arts*, 1817, and *Phil. Mag.*, li.

The following are the best authorities upon the subject of coloured glasses and artificial gems:—NERI, *Art de la Verrerie*; KUNCKEL; FONTANIEU, *Encyclopédie Méthodique*; *Ann. de Ch. et Ph.*, xiv. 57; AIKIN'S *Dictionary*, art. GLASS; LARDNER'S *Cyclopædia*; DUMAS' *Chim. app. aux Arts*.

CHAPTER VII.

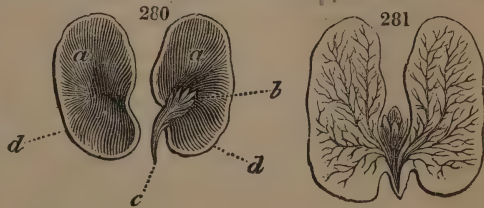
VEGETABLE PRODUCTS.

HAVING, in the preceding chapters, examined the elementary substances, and such of their combinations as are the result of artificial operations, we are now to turn our attention more exclusively to the *products of organization*. The present chapter embraces the interesting but complicated and difficult subject of *vegetable chemistry*, the objects of which are to inquire into the phenomena of vegetation, the nature of the ultimate elements of vegetable products, the proportions in which they combine, and the general laws which influence them; to examine the properties and distinctive chemical characters of the proximate components thence resulting, and the spontaneous changes to which they are subject.

The *chemical physiology of vegetables* constitutes an important branch of scientific botany, for which I must refer to physiological and botanical authors, want of space obliging me here to limit myself strictly to the enumeration of a few leading points which bear directly upon chemistry, and which are essentially connected with the theoretical and practical details upon which I must necessarily enter, or which have been touched upon in preceding pages.

§ I. OF THE GROWTH, STRUCTURE, AND FUNCTIONS OF PLANTS.

SEEDS, from which plants are originally derived, present infinite variety in form and character; without, however, adverting to the minute history of their different parts, we may here refer to the common *garden bean* as illustrating the general structure of a dicotyledonous seed, and as enabling us to refer generally to their functions and developement. This seed, when the external membranes or coverings are carefully removed, is easily separated into two distinct portions, which constitute the bulk of the seed, and which are termed the *cotyledons*; they are represented by *a a* in the annexed cut, fig. 280; between them is seen the *embryo* or *germ*, of which one portion *b*, lying between and within the cotyledons, is termed the *plumula*, and the small projecting part *c* is called the *radicle*.



When a seed is placed under favourable circumstances, the different parts begin to grow; the membranes burst, the plumula gradually expands, and rises to the surface of the soil, and the radicle puts forth ramifications, and becomes a root. These changes constitute *germination*. The cotyledons, originally insipid and farinaceous, become sweet and mucilaginous, and furnish materials for the early nutriment of the young plant, before

its root and leaves are adequate to their full functions; and vessels are observed for this purpose, as represented in fig. 281. When the root and stem have acquired a certain vigour, the cotyledons either rot away, or become leaves; and the plant then derives its nourishment by the root and leaves, the former collecting materials from the soil, the latter from the atmosphere.

The circumstances requisite for the healthy germination or growth of a seed are principally the following:—1. A due temperature, which is always above the freezing-point, and below 100° . 2. Moisture in due proportion. 3. A proper access of air, the oxygen of which is slowly converted into carbonic acid. The joint operation of these agents also is required: for seeds exposed to air and moisture, but kept below 32° , will not grow, though they are not injured by the low temperature: nor will a seed vegetate without air, though moisture be present, and a sufficient temperature; this is shown by burying seeds deep in the soil, and by the spontaneous vegetation upon newly-turned earth, in which seeds had existed, but through absence of oxygen had been unable to vegetate. Hence, in all cases of tillage, the seeds should be so sown as that the air may have access; in sandy soils this is easily attained, but in clay, the adhesiveness of the material becomes a source of sterility.

The swelling of the cotyledons is occasioned by the absorption of humidity; accordingly, all seeds enlarge in bulk when immersed in water, but those only of water-plants will *vegetate* under such circumstances; others require the more free access of air, and grow in the common soil at depths to which the atmosphere easily finds access, and which moisture easily percolates; but in these early stages of vegetable-development the soil is of no further use, for the seed will grow upon wet-paper, cloth, stone, or other materials; in short, air, moisture, and heat, are the only external requisites; everything else depending upon the seed itself. During the expansion and softening of the cotyledons, their albuminous and amylaceous parts become converted into gum and sugar, which are absorbed into the radicle, and contribute to its nourishment and growth into a root. When seeds are made to germinate in confined portions of air, it is found that they do not alter its bulk, but that a part of its oxygen is converted into carbonic acid; hence, one consequence of germination is a diminution in the relative proportion of carbon in the seed, leaving a comparative excess of hydrogen and oxygen, for these are its *ultimate* elements. This evolution of carbon is essential to the growth of the seed, for seeds will not germinate unless free oxygen be present: in hydrogen, nitrogen, and carbonic acid, when aided by moisture, the seed swells at first, but then decays; and in pure oxygen germination is morbidly accelerated; and it is said that certain oxidizing agents, especially the aqueous solution of chlorine, are effective in the restoration of the germinative power to old and dry seeds. All these changes are injuriously affected by *light*; sunshine soon kills the growing seeds, and even diffused day-light operates unpropitiously; we see, therefore, that in a properly-constituted soil, everything concurs in promoting the healthy functions of the seed; air, moisture, and heat, are duly administered, but the direct influence of light is excluded: darkness seems essential to its early development. At first, the *radicle* is most rapid in its growth; the nourishment

supplied by the cotyledons going chiefly, if not exclusively to it; it shoots forth its absorptive fibrils, which now take up nutriment from the soil, and feeding upon this, the plumula rises and puts forth *branches* and *leaves*, the profuse and even infinite variety of which may well excite our wonder and admiration, and is doubtlessly connected with ends and objects of which we at present are ignorant.

The general phenomena of the developement of a seed, are, chemically speaking, the same; but there are extraordinary modifications in the growth of plants derived from those which are *monocotyledonous*, as opposed to those derived from *dicotyledonous* or *polycotyledonous* seeds: the former class includes the *palm tribe*, and the greater proportion of tropical plants; all gramineous and liliaceous plants, likewise belong to it: their growth is *endogenous*, that is, it is the result of additions made internally; the latter class comprehends the ordinary forest-trees, and the greater number of our common vegetables; in them the growth is external, or *exogenous*; and the successive additions to their substance are made upon the exterior of the parts from which they proceed. The *palm-tree* furnishes an instance of endogenous growth: it bears a tuft of leaves at the top of a very lofty cylindrical stem, composed of a dense external layer of wood, and increasing in porosity towards the centre; its general texture appears similar throughout, and the distinctions of pith, wood, and bark, are not perceptible in its transverse section: its mode of growth is peculiar; it first forms a circle of leaves, which after having attained a certain size, are succeeded by another circle growing from the interior of the former: these are reproduced annually, each crop exerting an outward pressure upon the ligneous formation of the preceding year, which at length becomes too dense to admit of further distension: the growth of the inner layers is then necessarily directed upwards, so that they each successively rise by distinct stages, always proceeding from the interior; but the stem never increasing in diameter after the consolidation of its exterior layer. A disc of leaves shoots yearly from the new layer of wood, and when these fall off they leave a circular mark upon the stem, so that the age of the tree may be judged of by the number of these alternations of circular knots. Similar appearances may be observed upon grasses.

The section of a *bicotyledonous* tree, or one of *exogenous* growth, exhibits several distinct formations: there is a central *pith*, the structure of which is cellular or spongy, and not tubular, and which is liable to much variation in quantity and character in different plants or trees, and at different stages of their growth: it is surrounded by concentric layers of *wood*, the exterior portions of which are softer than the interior; hence the distinction into *alburnum* or *new-wood*, and *duramen* or *heart-wood*, the former being paler than the latter, which is often brown, and in ebony, black. The wood is enveloped by the *bark*, which consists also of concentric layers, of which the innermost bears the name of *liber*; the whole is covered by *cellular tissue* and *epidermis*: the bark, like the wood, when more than one year old, is composed of as many layers of cellular integument and woody fibre as it is years old, the former being external, and the latter internal, in each layer, and every layer being formed beneath the previous one, and therefore next the wood: so that

the bark is to a certain extent elastic or distensible; but after a time it splits, as in the *elm*, the *cork*, and the generality of European trees; or it peels off, as in the *plane* and *birch*. In the spring of the year a viscid substance is found between the bark and the wood, which is termed *cam-bium*. Besides these distinct formations which trees of exogenous growth present, the horizontal section of the stem exhibits a number of rays or lines proceeding from the pith to the circumference; they are apparently composed of one or more layers of cellular tissue, and are termed *medullary rays*; in longitudinal section they give to many woods a peculiar satiny lustre. As a new layer of wood and bark are formed annually, it is customary to judge of the age of trees by the number of concentric rings which either of them exhibits; but these calculations are open to many fallacies. (See LINDLEY'S *Introd. to Botany*, book i., chap. ii.)

The *cuticle*, or most superficial membrane of plants, is extremely varied in different vegetables, and in different parts of the same plant: it extends over every part of the plant; it allows, by its pores, or *stomata*, of absorption and transpiration, and being generally transparent, at least upon the leaves and flowers, it admits the influence of light. The cuticle varies in texture and appearance in different plants. On the currant and elder tree, it is smooth, and scales off: on the fruit of the peach, and on the leaf of the mullein, it is covered with wool; on the leaf of the white willow, it is silky; in several plants, it is covered with hair and bristles, which in the nettle are perforated, and contain a venomous fluid: on the plum and upon many leaves, it is varnished with a resinous exudation, which prevents injury from rain: it is fungous on the bark of the cork-tree; and on grasses, on the equisetum, and especially on different species of the rattan, it is covered with a glassy net-work of silica. This fact first occurred to Sir H. Davy in 1798, and led to experiments by which he ascertained that siliceous earth existed generally in the epidermis of the hollow plants. "It serves," he observes, "as a support, protects the bark from the action of insects, and seems to perform a part in the economy of those feeble vegetable tribes, similar to that performed in the animal kingdom by the shell of the crustaceous insects." Silica is also found in the hollow stem of the bamboo, constituting the substance called *tabasheer*. It is to the large quantity of silica existing in grasses, that the glassy character of the products of burned hay and corn stacks is to be attributed.

Under the cuticle, or epidermis, is the *parenchyma*; a soft substance, appearing under the microscope of a honeycombed or hexagonal cellular structure, resulting from the mechanical laws which influence the pressure of soft cylinders.

As the tree grows, the stem and the root both send out their branches or ramifications, and the phenomena of their production are extremely curious and interesting: the branches, and their subdivisions, are generally produced with remarkable regularity, so as to give a defined outline to the shrub or tree, except where unequal exposure to air, light, or heat, causes one side to expand more luxuriantly than the other: the root, too, in an uniform soil, extends equally on all sides, but various causes likewise interfere with its growth, and it sometimes presents very extraordinary diversions from its usual progress.

I have already noticed the infinitely-varied forms and textures of the *leaves* of plants; their anatomy has been closely investigated by botanists as well as the mode of their growth or formation; they for the most part exhibit a beautiful skeleton or frame-work of ligneous fibre, supporting a delicate vascular and cellular structure, and are covered by cuticle. The *flowers*, and their parts, are analogous in anatomical structure.

Besides the *cells*, which have been mentioned as constituting a large proportion of the vegetable texture, there also are membranous *tubes* interspersed through their various parts, which exhibit extraordinary varieties in their form, characters, and dimensions; some are simple, others jointed, or spiral, or annular, or perforated; their contents also, as well as those of the cells, are very various; they contain crude or concocted sap, various secretions, or products of vegetation, and air.

The *nourishment of plants* is partly derived from the soil, through the medium of the roots, and partly from the air, by means of the leaves. In spring, before the leaves appear, the roots are chiefly active, and absorb carbonic acid, ammonia, and other matters derived from the soil, and from the decay of the fallen leaves of the preceding autumn. The absorptive power of the root is not merely capillary, but peculiar and vital, and seems to reside in the terminal fibres or *spongioles*, and not in the radicular branches generally; hence the injury which is generally inflicted upon the root by removal or transplantation; the necessity of carrying with the root a sufficient ball of earth to prevent the abrasion or fracture of the spongioles; and the advantage of growing plants in pots, which are intended afterwards to be removed into the border. The roots absorb some substances more readily than others, but they have no selective power in respect to the most appropriate nutriment; and Saussure has shown that they, in many instances, absorb poisonous substances more rapidly than others. Marce's experiments have taught us that white arsenic and corrosive sublimate are poisonous to vegetables as well as to animals; and that vegetable poisons are equally active, such as opium and prussic acid, which when applied, even in very dilute solution, to the roots, cause the plant to droop and die. It has been ascertained that the access of air to the roots of plants is not only not prejudicial, but that it favours the healthy performance of their functions.

The fluids which are absorbed by the roots of plants, constitute the *crude* or *ascending sap**; they are circulated in appropriate vessels throughout the vegetable fabric, being transmitted more copiously to some organs than to others, and contribute to the formation of new parts, and to the composition of their various secretions. Hales, long ago, demonstrated the power with which the sap ascends in its vessels, and

* The sap of plants is of very various composition, and contains, besides certain proximate vegetable principles, several saline substances, especially the acetates of potassa and of lime: it also often exhibits traces of uncombined vegetable acids. The sap of the elm, beech, hornbeam, and birch, have been examined by Vauquelin (*Ann. de Chim.*, xxxi.): he found extractive and mucila-

ginous matter, and acetic acid combined with potassa and lime. The solid matter afforded by their evaporation, yielded an ammoniacal smell, probably owing to albumen: the sap of the birch afforded saccharine matter. Dr. Prout has given some account of the sap of the vine. Its taste is sweetish, and its specific gravity scarcely exceeded that of water. Potassa and ammonia reddened it, and precipi-

endeavoured to account for the rapidity and the direction of its progress; but this phenomenon is still unexplained: a valvular system in the vessels, somewhat similar to that of the veins of animals, was presumed to be efficient in preventing the retrograde motion of the sap: but the well-known fact, that a plant may be inverted, and that the branches may be made roots and the roots branches, subverts such an hypothesis. When the sap has once entered its vessels, it seems invariably to tend (perhaps in the direction of least resistance) towards the *leaves*, which, as regards its chemical changes and elaboration, are certainly most important and essential organs. The quantity of the sap which, in many plants, is thus carried upwards from the roots, is very surprising, considering the source whence it must be derived; it may often be abundantly collected by cutting off a branch of a young and thriving tree or shrub, and it is then seen to ooze from the section, flowing over in drops, and running down the stem. The vast evaporation, also, that takes place by the leaves, must be chiefly, if not exclusively, supplied by the roots. Many plants, examined by Woodward, lost, in three months, one hundred times their own weight of water by transpiration. Hales found a sun-flower lose one pound four ounces, and a cabbage one pound three ounces, in twenty-four hours, by this process. This perspiration is said to depend upon the number of the *stomata*, and therefore to be less in evergreens, in which they are few, than in deciduous and herbaceous plants. Whenever the balance between the absorptive power of the spongioles and the emissive power of the leaves is disturbed, the plant suffers, as we see by the drooping of the leaves in a warm and dry atmosphere on the one hand, and in a dry soil on the other.

The leaves are the seat of the most important vegetable functions; they are organs of absorption and emission, of nutrition and of digestion. The sap which in its crude state, as it rises from the roots, is extremely dilute, and consists of little else than water, with carbonic acid, and traces of saline matter, is concentrated by evaporation in the leaves, and receives an addition of carbon from the carbonic acid in the atmosphere; air, and light, and heat, are active in these changes, and the leaves are admirably adapted to such complicated purposes. Their influence in modifying the composition of the sap, and in supplying food to all parts

tated red flocks soluble in acetic acid. It was rendered slightly turbid by nitrate of silver, subacetate of lead, ferrocyanuret of potassium, and oxalate of ammonia. It contained carbonic and acetic acids, and an alkali. (*Ann. of Phil.*, v.) Professor Scherer analyzed the sap of the common maple: it had a milky appearance, and sweet taste. It did not affect litmus or turmeric. It was precipitated by oxalate of potassa, nitrate of silver, and baryta-water. When evaporated, it yielded a salt with base of lime, containing a peculiar acid, which he calls *aceric acid*. (*SCHWEIGGER'S Journal*, iv.)

The sap of the rose-tree has been examined by Mr. Addams. (*Quarterly*

Journal, iv. 147, N.S.) In twelve fluid ounces he found

Oxalate of lime . . .	2·900
Acetate of lime . . .	1·097
Acetate of potassa . .	0·700
Gum and extractive .	2·100
Sugar, &c. (soluble in } alcohol) }	0·100
Loss	0·353
	7·250

It is, however, almost impossible to collect the ascending sap without admixture of some other juices of the plant, so that the analyses only afford approximations to its real composition.

about them, is shown by the mischief which ensues when they are removed; and we have evidence of their emissive or perspiratory powers in the watery vapour which they give off, and which sometimes collects in drops; they also occasionally secrete grosser compounds. If we place a healthy leaf between two cold plates of glass, we generally observe that the greatest visible transpiration is from the lower surface, and the organization of the leaf is apparently such as to render that surface the most apt for the escape of watery vapour: but in some plants the upper surfaces of the leaves are said to be most active, so that probably both the absorptive and excretive power of the leaves varies in different individuals.

One of the most curious and important functions of the leaves is their power of decomposing the carbonic acid which is always present in the air, retaining its carbon, or a portion of it, and emitting pure oxygen; and to show how important an agent light is in inducing these chemical changes, it is found that they only go on under its influence, and that in the dark they are either inactive, or even deteriorate the air (as we are in the habit of saying,) by the addition of carbonic acid; upon the whole, however, although different plants act very differently in this respect, there can be no doubt that the influence of the vegetable creation upon the atmosphere is purificative; that is, that part of the carbonic acid produced by animal respiration, and by combustion and other causes, is decomposed by the leaves, and that they evolve more oxygen during the day-time than carbonic acid during the night. This is well illustrated by Dr. Priestley's experiments on the sprigs of mint already cited (p. 65). We now, also, shall duly appreciate the importance of aqueous vapour, and of carbonic acid, as components of the atmosphere (p. 453), for that the leaves often absorb moisture from the air is shown by the reviving influence of damp air upon a drooping plant, or of the direct application of water to its leaves. It has also been proved that no oxygen is evolved by plants, except carbonic acid be present in the air. Aquatic plants furnish a striking corroboration of these observations; they decompose the carbonic acid of the air in water, and evolve oxygen during the influence of light; this carbonic acid may be furnished from various sources, but part of it is often derived from the respiration of fishes, and would accumulate to a noxious extent were it not replaced by the oxygen emitted by the plants; hence it is that fish never thrive in waters which are exempt from vegetation; and that in ornamental vases and basins, in which there are fish, aquatic plants are at the same time desirable. But, although plants will not thrive without access to carbonic acid, its excess is prejudicial, and it has been found to operate as a poison when it exceeds one-twelfth of the atmospheric air; in such proportion, however, it never exists in the free atmosphere.

Saussure's experiments upon the functions of the leaves have taught us the curious fact, that along with the carbon, a portion of oxygen is also absorbed, and this (in the absence of light) from an atmosphere not containing carbonic acid. Fresh leaves, exposed *in the dark* under a bell-glass of air, absorb one portion of oxygen, and convert another into carbonic acid: if afterwards *exposed to the light*, and especially to the direct rays of the sun, they re-absorb the carbon, and give out the whole

of the oxygen, gradually restoring the air to its pristine condition. Very succulent leaves (those of the *Cactus opuntia* for instance), absorb oxygen in the dark, and again evolve it in the light: in the course of 30 hours they thus absorbed more than their own bulk, and it could not be extracted from them either by warmth, or by exposing them in the vacuum of the air-pump, though in the sun's rays they invariably emitted it. These properties belong to the leaves of all plants, but the effects vary much in degree in different genera; they are also probably more or less resident in all the *green parts* of vegetables, but are not possessed by the bark or roots. Boussingault has published an elaborate paper in the *Ann. de Chim. et Phys.* (Lxix. 5 and 353), respecting the absorption of nitrogen by the leaves of plants, but the question is not satisfactorily decided.

The changes which the sap undergoes in the leaves are extremely complicated, and are sometimes manifest in their obvious properties; thus, the leaves of some species of *Bryophyllum*, are said to be sour in the morning, tasteless at noon, and bitter at night, reddening litmus at one time of the day and not at another; the flowers of the *Cichorium intibus* are white or blue, according to the intensity of the day-light; and many fruits are observed to be more acid in the morning than in the evening.

The circulation of the sap, as has been before remarked, is involved, as to its cause, in great obscurity, and even the general direction of its progress in the growing vegetable has not been very satisfactorily ascertained; but the researches of Andrew Knight (*Phil. Trans.*, 1801), and other experimental physiologists, render it probable, that the chief ascent of the sap from the roots to the leaves, is in the vascular system of the *alburnum* and outer layers of wood, that it is thence transferred into the leaves, and that having there undergone changes, some of which have been adverted to, it descends chiefly, but not exclusively, by the *liber* or inner layer of bark, giving rise to the secretion of *cambium*, to the formation of new wood, and to the deposition or separation of gum, resin, and other characteristic proximate principles. The proofs of this circulation of the sap are, that if a branch be cut through in the spring, sap will exude more or less from its whole surface, but most copiously from the *alburnum*; if it be cut half through, and a semicylindrical piece removed, the principal exudation of sap upon the upper half will then be in the inner layers of the bark, and the liquid which there oozes will be different from, and more concentrated than that which runs from the outer layers of the wood; as if the *ascending sap-vessels* had been divided in the *alburnum*, and the descending in the *liber*; and if a ring of bark be carefully removed from a branch of a young tree early in the spring, the portion above the section will be turgid, and perhaps bear blossom and fruit, indicating symptoms of accumulation of sap, the escape of which from the cut surface is soon prevented by the induration of the inspissated descending sap, and ultimately by the growth of new ligneous matter, the proportion of which is enormous upon the *upper*, as compared with that upon the under line of section. This explains the influence of *ringing* the branches of fruit trees, with a view of rendering them productive; and the difference between the ringed and the other branches is

often very striking, late in the season, as affecting the fruit, leaves, and general aspect of the plethoric parts.

Plants are in general extremely susceptible of impurities in the air that surrounds them; slight modifications, therefore, in the composition of the atmosphere, are more or less prejudicial to their growth; especially when not under the influence of light: thus, although in the sun, a plant will thrive in air containing 8 or 10 per cent. of carbonic acid, such excess of that gas is fatal to it in the shade. The experiments of Drs. Christison and Turner upon this subject (*BREWSTER'S Journal*, 1828, and *LINDLEY'S Introduction*, book ii. ch. v.) are very instructive; and instead of being surprised at the injury which plants sustain in the atmosphere of London, lead us to wonder that they are not more generally affected by it; there is no doubt, however, that plants, like animals, vary in regard to the delicacy of their constitutions, and that some are infinitely more susceptible, not only of changes in the temperature and humidity of the air, than others, but are fatally influenced by the presence of foreign matters which more hardy tribes resist. Dr. Macculloch has given us some curious facts upon this subject. (*Quarterly Journal of Science* for 1829.)

The influence of the *flowers* of plants upon the atmosphere, is probably as various as are their infinitely-varied forms, colours, odours, and composition; even in the light, they invariably deteriorate the air; that is, they convert a portion of its oxygen into carbonic acid, and that, more rapidly than the leaves are found to do, in the dark: the sexual organs of the flower have been shown by Saussure materially to influence the destruction of oxygen. From M. Berard's experiments on the action of *fruits* upon air (*Ann de Ch. et Ph.*, xvi.), it appears that they, in all cases, tend to the production of carbonic acid, and that this loss of carbon is essential to the ripening of the fruit; for when deprived of oxygen, the fruit dies. When fruits rot, they first change a portion of the surrounding oxygen into carbonic acid, and then liberate the same gas ready formed. He considers gum and lignin as the principles in unripe fruits which chiefly tend to the formation of sugar during their ripening, and has given several analyses of fruits in illustration of these views, a few of which are selected in the following Table: the elements of water are also probably concerned in the change.

	CHERRIES.		PLUMS.		PEACHES.		PEARS.		APRICOTS.		
	Green.	Ripe.	Green.	Ripe.	Green.	Ripe.	Green.	Ripe.	Green.	Riper.	Ripe.
Vegetable albumen	0.21	0.57	0.45	0.28	0.41	0.93	0.08	0.21	0.76	0.34	0.17
Colouring matter	0.05	..	0.03	0.08	0.27	..	0.08	0.01	0.04	0.03	0.10
Lignin . .	2.44	1.12	1.26	1.11	3.01	1.21	3.80	2.16	3.61	2.53	1.86
Gum . .	6.01	3.23	5.53	2.06	4.22	4.85	3.17	2.07	4.10	4.47	5.12
Sugar . .	1.12	18.12	17.71	24.81	0.63	11.61	6.45	11.52	Trace	6.64	16.48
Malic acid	1.75	2.01	0.45	0.56	1.07	1.10	0.11	0.08	2.70	2.30	1.80
Lime . .	0.14	0.10	Traces	Traces	0.08	0.06	0.03	0.04	Trace	Trace	Trace
Water . .	88.28	74.85	74.57	71.10	90.31	80.24	86.28	83.88	89.39	84.49	74.87

The evolution of *heat* during the germination of seeds, is well shown by the rise of temperature in the process of malting; and the temperature of the organs of the flower, during the period of their activity, is, in some plants, many degrees above that of the atmosphere: these cases of the production of heat must not be confounded with those of fermentation; they are perfectly distinct, especially in the latter case. It appears probable that all plants have a power, dependent upon their vitality, of maintaining, to a certain extent, an equable temperature; but how far their internal heat can be affected by external causes, has not as yet been satisfactorily ascertained.

I have now briefly enumerated a few of those phenomena of vegetation in which chemical changes are principally concerned; the whole inquiry is full of interest to the chemical physiologist. Among the *vital powers* of plants, there are some which I have not adverted to, because apparently unconnected with the subject before us; such as the *sleep* of plants; the expansion and contraction of their flowers and leaves, dependent upon the presence or absence of light; their spontaneous and their involuntary motions, as in the *Hedysarum gyrans*, the *Mimosa pudica*, the *Dionæa muscipula*, and the influence of electricity upon the latter.

It has been stated that carbon, oxygen, hydrogen, and nitrogen, are the essential ultimate elements of vegetable products, and it is evident that they derive a part of their carbon and oxygen from the air: the source of their hydrogen and nitrogen is probably acquired in the form of ammonia. That plants derive much of their nutriment from the soil, is obvious from its impoverishment, and from the direct influence of nourishment so applied; the substances thus taken up, are, or at least may be, very complicated, consisting of a variety of soluble matters, of inorganic as well as of organic origin; and the rapidity or facility with which they are imbibed depend upon a variety of obscure causes, and partly upon the relative magnitude and absorbent powers of the leaves; for it is, I believe, admitted, that plants with large systems of leaves absorb less from the soil than those which are less liberally provided with foliage; and, independent of this, some plants are certainly more voracious and gross feeders than others, thriving in proportion to the richness of the soil, and acquiring odour and flavour from the manure with which they are supplied.

Manures are of *vegetable*, *animal*, or *mineral* origin. The two former are capable of affording carbon, nitrogen, and hydrogen; they may also yield some of the immediate principles of vegetables. The mere existence, however, of organic matter in the soil is not sufficient to constitute it a *manure*; it must be reduced to a state in which it can be absorbed by the roots of a growing vegetable; this is effected by fermentation or putrefaction. Where the vegetable matter is in an inert insoluble form, it will be of no avail unless rendered active and soluble, which is effected either by mixing it with such kinds of animal matter as undergo quick putrefaction, such, for instance, as dung, rotten fish, or decaying parts of animals; or, by the operation of alkaline bodies, such as quicklime, &c. When newly-burned lime is strewed over a soil containing inert vegetable matter, it acts upon it, and renders it more or less decomposable,

while the lime, by absorbing moisture and carbonic acid, is slaked, and passes into the state of chalk, which is often a useful addition to the soil: but when limestone contains magnesia, it remains caustic, and sometimes proves injurious.

The limits of this volume prevent my enlarging upon these topics, which are full of interest, and demand a separate work for their illustration. Such a work Sir H. Davy published several years ago, but the general progress of the science, since that time, has been such as materially to affect all its collateral branches; and the views and doctrines that were then plausible, now require revision and modification. The most recent work in which these matters are discussed at length is the Introduction to LIEBIG'S *Traité de Chimie Organique*.

Having now noticed a few of the leading facts connected with the structure and growth of plants, which bear upon their chemical physiology, I shall proceed to the methods of analysis applicable to the discovery of their ultimate elements, and to the proportions in which they are combined in their proximate or immediate principles.

§ II. OF THE COMPOSITION AND ANALYSIS OF VEGETABLE SUBSTANCES, AND OF THEIR ULTIMATE PRINCIPLES.

ALTHOUGH the *ultimate principles* of vegetable substances are few in number, yet by being combined in various proportions, they give rise to a series of compounds materially differing from each other, and which are called their *proximate components*. It has just been stated that *carbon, hydrogen, oxygen, and nitrogen*, are the principal ultimate components of vegetables; in some there are traces of sulphur; and in their sap or juices we find small proportions of potassa and of lime, and sometimes of soda and of magnesia: these bodies are combined with acids, and are chiefly obtained by burning or incineration. It has already been said that some plants contain silica; sulphate of lime is found in clover; nitrate of potassa in the sap of the sun-flower; and nitrate of soda in barley. Common salt, and some other chlorides, are frequent ingredients in marine plants; phosphate of lime is found in oats and some other seeds; and nearly all vegetables yield traces of oxide of iron, and many of oxide of manganese. In SAUSSURE'S *Chemical Researches on Vegetation*, and in THOMSON'S *System of Chemistry*, are copious tables, showing the earthy and saline constituents of vegetables.

But the elements with which we shall almost exclusively have to deal, in our examination of vegetable products, are the four first, and the number, and the varied characters, of the compounds to which they give rise under the influence of organization, is certainly most extraordinary; of this diversity, some of the causes will become apparent as we proceed; others have not only repulsed all attempts at explanation, but even baffle our most unlimited conjectures.

There is another leading distinction between *organic* and *inorganic* compounds, which is, that in the *latter* the elements are generally united in *binary* arrangements; thus, *crystallized sulphate of soda* is composed of sulphuric acid, soda, and water, which are *binary* compounds of sulphur and oxygen, sodium and oxygen, and hydrogen and oxygen, &c.: but

organic products are *ternary* or *quaternary* combinations, which we can scarcely ever imitate by artificial processes; and in the formation of which a greater number of simple atoms are usually concerned: sulphuric acid, for instance, is a compound of 1 atom of sulphur, and 3 of oxygen; but *tartaric acid* consists of 4 atoms of carbon, 2 of hydrogen, and 5 of oxygen; hence, in organic compounds, the proximate atoms are heavier, or the equivalents larger, and the saturating powers less, than in inorganic combinations: there are, however, some instances of binary organic compounds; caoutchouc, and some oils, are composed only of carbon and hydrogen; but then there is this distinction, that they do not consist of one atom of the one element united to one or more of the other, but several atoms of each element are combined; and in most cases, no simple relation between them can be observed.

No peculiarity of organic combination is more remarkable than the extreme *difference* between substances constituted of *similar* elements; sugar, gum, &c., consist of carbon, hydrogen, and oxygen; but those substances have neither the characters of acids or bases; acetic, succinic, citric, and formic *acids* also consist of the same elements, but in different proportions or differently congregated. Oxalic acid presents a striking peculiarity; it is composed of carbon and oxygen only, and contains less oxygen than carbonic acid, and yet is one of the most powerful acids; it is either a direct product of organization, or obtained indirectly from other organized compounds.

If, therefore, we endeavour to combine the elements of organic bodies by *artificial* operations, they show a tendency to pass into binary, and not into ternary or quaternary compounds; and even in the living body, products that have already been organized, appear essential to the formation of new ones; thus, vegetable life is in a great measure supported by the decay of former vegetables; and graminivorous and carnivorous animals require vegetable and animal substances for their sustenance; for although it be true that carbon, hydrogen, oxygen, and nitrogen, are the ultimate elements of our food, we should soon starve upon charcoal, and water, and nitrogen, or upon any of their compounds *which had not already gone through the process of organization*.

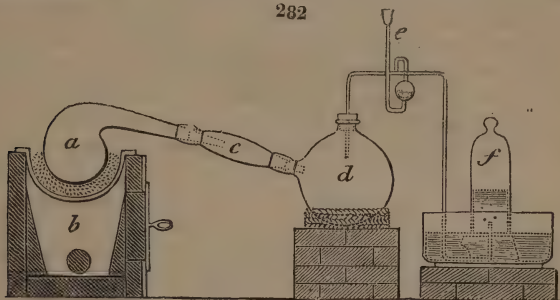
As, therefore, we cannot so combine the insulated inorganic elements as to imitate the products of organization, we are deprived, in our researches upon these forms of matter, of the aid of *synthetic* proof, in the ordinary acceptation, at least, of that term; and in determining the nature and the relative proportions of the elements of organic compounds, we are limited to *analytic* operations; and even in them (as we shall presently find) numerous difficulties occur, especially affecting the determination of the integral atomic weights of the compounds, and the theory of their elementary arrangements.

The first attempts at the analysis of vegetable substances, consisted in subjecting them to *destructive distillation*, and this method was greatly extended and improved by Hales, Priestley, and the earlier pneumatic chemists, who paid especial attention to the gaseous products of such operations, which, together with aqueous and oily liquids, and a residue of carbon, constitute the results of the process; hence the conclusion of the older chemists, that air, oil, water, and *earth*, including under that

name the carbonaceous residue (or *caput mortuum*, as they called it), were the universal *elements* of organic bodies. It is, however, evident that most of these are secondary results, that they are *products* of the operation; and accordingly their composition and relative proportions are liable to infinite variation, dependent upon the manner in which the distillation has been effected. In modern analysis, therefore, this method is rejected; or at least only adopted where some specific product is to be examined, or where some general inference is to be drawn from the nature or proportions of the newly-produced compounds: *ammonia*, for instance, denotes the presence of nitrogen; a large quantity of oil announces excess of hydrogen; and of *acid* excess of *oxygen*; the uncondensed *gases*, and the residuary *carbon* may also be examined.

The following is a form of apparatus in which these operations may be carried on:—

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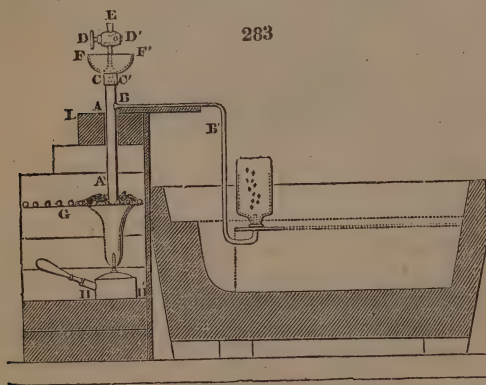


a is a luted glass or earthen retort, containing the substance to be decomposed, and placed in a sand-heat *b*, which is gradually raised to a red heat. It is connected by the adapter *c* with the receiver *d*, which is kept cool for the condensation of the liquid products; the gases pass into the bell-glass *f* standing over water or mercury. *e* is a *tube of safety*, to allow for sudden expansion or contraction; there being in its lower part a small quantity of mercury which is occasionally elevated or depressed. The joints are secured by strips of bladder.

If we again refer to the nature of the *ultimate elements* of organic bodies, it is obvious that combustion in oxygen will enable us to determine their relative proportions. To take the simplest instance, let us suppose the subject of analysis to consist of *carbon* and *hydrogen* only; in that case the products of its entire and perfect combustion in excess of oxygen would be *carbonic acid* and *water*; the quantity of *carbonic acid* being determined, that of the *carbon* which had formed it might be inferred; and this ascertained, and compared with the *original weight* of the substance, would give the proportion of *hydrogen*: thus, supposing 7 grains of the substance under examination yielded, by combustion in oxygen, 22 grains of carbonic acid, it would have consisted of 6 carbon + 1 hydrogen; for 22 carbonic acid (consisting of 6 carbon + 16 oxygen) are equivalent to 6 carbon. If the subject of analysis were a compound of carbon, hydrogen, and oxygen, it might be expedient to determine the weight of the produced *water*, with a view of arriving at that of the hydrogen. Let us suppose 15 grains of a compound of carbon, hydrogen,

and oxygen, to afford 22 grains of carbonic acid, and 9 of water; then we should again have 6 of carbon, and 1 of hydrogen, (for 9 water = 1 hydrogen and 8 oxygen,) and there would be a deficiency of 8 grains, (required to make up the original 15,) which would be the inferred weight of the oxygen. When *nitrogen* is present, its quantitative determination requires precautions to which I shall presently advert. So far, therefore, the mere *theory* of these ultimate analyses by combustion, is sufficiently simple, but the difficulties of *manipulation* are numerous and considerable; they relate, first, to the mode of effecting the *entire* combustion of the organic compound, and secondly, to the accurate collection and quantitative determination of the *products* of combustion*.

Gay Lussac and Thenard (*Recherches Physico-Chimiques*, tom ii.) were the first who endeavoured to meet these difficulties, and to furnish accurate analyses, upon the principles just stated. The method of effecting the combustion of an organic product in oxygen, which they originally adopted, consisted in forming a given weight of it into one or more pellets, with a requisite proportion of *chlorate of potassa*, and then subjecting it to a red heat. An account of their process is given in THENARD'S *Traité de Chimie*, with the following arrangement and description of the apparatus. A hole is made through a brick L, and



the glass tube AA' is passed through it as far as to the small lateral tube BB', which passes into the mercurial trough. The lower extremity of the tube rests upon the grate G, where it is to be heated red-hot by charcoal inflamed by the lamp H. A brass cock is fitted, by grinding, to the tube cc'. It has a solid plug dd',

in which is a cavity large enough to contain one of the balls to be analyzed, and which is introduced at the opening E. The plug is then turned round, and the ball falls into the red-hot part of the tube, where it burns, the gases passing into the mercurial apparatus. FF' is a basin, into which ice may be introduced to keep the metallic parts of the apparatus cool. It is convenient to case the lower part of the tube A in iron, as it is sometimes blown out at that part by the expansion within.

I shall not advert to the further proceedings with this apparatus, because it is rarely used. The chlorate of potassa is objectionable,

* I have not space here to go into the many details connected with this difficult subject, which, indeed, can only be learned in the laboratory: my object is to give the reader such an outline of the proceedings as may prevent the necessity of recurring to them in the individual

analyses that I shall afterwards have to refer to, and may render the *data* upon which they are founded intelligible. The fifth volume of DUMAS' *Chimie appliquée aux Arts*, may be profitably consulted for more minute particulars; as also, the authors to which I refer in the text.

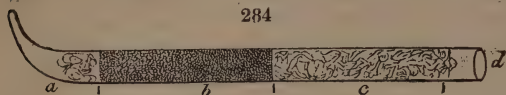
because, except in particular cases, *perfect combustion* cannot be ensured by it; that is, the evolved gas is too suddenly generated, and is never perfectly *inodorous*, and in these analyses there should not be the smallest residuary vestige of the organic product appreciable by the empyreumatic smell of the produced carbonic acid or aqueous vapour.

To avoid the imperfections of this method, Gay Lussac suggested the employment of *oxide of copper* as a source of oxygen for the combustion, and it has the advantage of resisting decomposition when heated alone, whilst it readily yields oxygen to carbon and hydrogen, at high temperatures; so that by weighing it before and after the analysis, the quantity of oxygen imparted to the combustible may, if requisite, be determined. The analysis, therefore, as now practised, consists in mixing the organic matter in due proportion with oxide of copper, and so subjecting it to combustion, that the carbon may be entirely converted into *carbonic acid*, and the hydrogen into *water*. When nitrogen is present it is collected in the state of *gas*, and the proportion of oxygen is estimated by the deficiency in the joint weights of the carbon, hydrogen, and nitrogen, as compared with the original weight of the portion of the organic product subjected to analysis.

The oxide of copper is best obtained by heating copper-shavings to redness, exposed to air, and then bruising them in a mortar, by which the oxide is separated, and may be sifted off; or the plates may be successively quenched in water, when the scales of oxide fall off, and may be dried, powdered, and heated to redness. The oxide derived from the ignition of nitrate of copper is sometimes preferable, as being finer and lighter than the preceding; as these oxides are *hygrometric*, they should be kept in stopper-phials, and used warm, with as little exposure to air as possible.

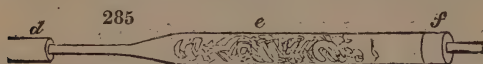
The tubes used in these analyses should be of green glass, and generally about three-tenths of an inch in diameter, and from 15 to 18 inches in length, sealed, and either drawn into a point, or rounded at the sealed end: the open extremity should be smoothed by fusion so as to receive a cork without danger of cracking; and it is generally proper to protect the tube, by rolling a strip of thick copper-leaf spirally round it, tied at each end by a piece of wire. It may be heated either by means of Cooper's lamp-furnace, (*Quart. Jour.*, xvii. 22,) or over charcoal, in a temporary arrangement of a grate and fire-bricks, (*FARADAY'S Manipul.*), but all these arrangements must be left to the management of the operator, and require varying according to circumstances, only care must be taken that they are such as to enable us to heat successive portions of the tube at one time, and at another to give its whole length a red heat. (*DUMAS*, v.) The whole of this process will essentially vary in its details according to the peculiarities of the product under examination, which, if *liquid*, requires also further modifications of the apparatus: for these I must refer to the details given by Dumas, and to a paper upon the subject by Liebig, in the 21st volume of *POGGENDORFF'S Annalen*. If *solid*, 3 or 4 grains of it, accurately weighed, and dried at 212° in vacuo over sulphuric acid, (see the means of effecting this described by Dr. *PROUT*, *Ann. of Phil.*, vi. 272,) are mixed with about 200 grains of the oxide of copper, and introduced into the analyzing-

tube, into the end of which is previously placed about half an inch in length of small copper shavings superficially oxidized; these shavings should also occupy about two inches of the tube *above*, or, as it lies horizontally, *before* the organic mixture, the object being to keep the whole contents of the tube in a loose or porous condition, so that the



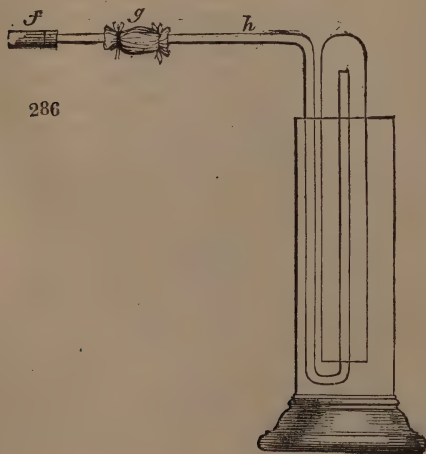
gaseous products may escape from it without impediment. Perhaps the annexed sketch may render this arrangement

more intelligible, in which *a* represents the sealed end containing oxidized copper-turnings, or fragments of the oxide; *b*, the intimate mixture of the oxide with the organic substance, and *c*, the remaining portion of the tube containing turnings, or scales of oxide. In this case, the portion *c* is first heated to redness, and the heat is then gradually extended through *b* towards *a*, in such a manner, that all the products may have to traverse the heated oxide, for perfect and entire destruction of the matter subjected to experiment is the essential part of the process. Let us now suppose that the organic substance under examination is a ternary compound of hydrogen, carbon, and oxygen; it is obvious that the products will be *water* and *carbonic acid*: to ascertain the weight of the former, and thence the weight of the *hydrogen* required to form it, the products, as they escape from *d*, may be carried through a tube containing fragments of fused chloride of calcium, and accurately weighed; by this, the vapour of water will be absorbed, and the increase in the *weight* of the tube and its contents, will indicate its quantity: every 9 grains of increase are equivalent to 1 grain of hydrogen. In the following cut (fig. 285), *d* represents



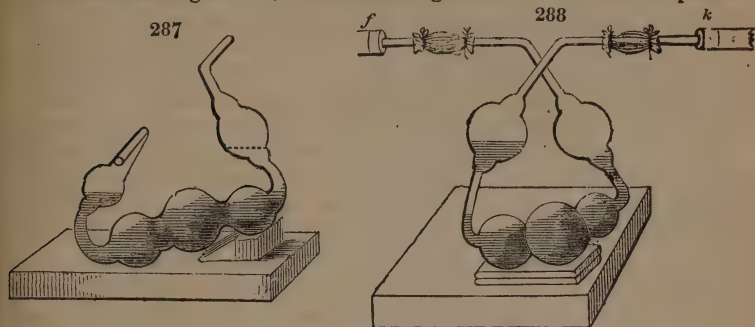
the end of the decomposing tube (fig. 284), to which is annexed the chloride of calcium tube

e, from which issues the smaller tube *f*; the junction at *d* is made airtight by perforated cork. The weight of the produced carbonic acid may



be learned in two ways; either by collecting it in its gaseous state, and determining its bulk, and thence deducing its weight and that of the carbon which it contains; or by condensing it into a weighed solution of caustic potassa, and determining its quantity directly, by the increase of weight sustained by the solution. In the former case, the tube at *f* (fig. 286), is connected by the caoutchouc joint *g*, with the bent-tube *h*, the extremity of which terminates in the inverted graduated jar *i*, filled with mercury.

In the latter case, the carbonic acid gas may be conducted from the extremity of the chloride of calcium tube *f*, into the apparatus represented in the annexed cut (fig. 287), which is a glass tube blown into several thin bulbular enlargements, and containing a solution of caustic potassa.



In fig. 288, this condenser is shown connected with the chloride of calcium tube *f*, by short lengths of caoutchouc piping, and having another tube *k*, containing fragments of fused potassa, attached in the same way to its other extremity. This latter tube is only required where *nitrogen* is to be collected, and even then, as I shall presently state, may be dispensed with*.

It will now, I think, be obvious, that after the abstraction of the *water*, in the chloride of calcium tube, the carbonic acid will pass on into the solution of caustic potassa, through which, by properly inclining the apparatus, it may be made to pass in divided bubbles, and under some pressure, so as to ensure its total absorption. When the experiment is completed, the apparatus is allowed to cool, and in order to prevent any portion of the alkaline solution retrograding into the chloride tube, the tip of the analyzing-tube near *a* (fig. 284), is broken off, and any residuary carbonic acid may then be drawn into the alkaline solution, by applying gentle suction at the end of the tube *k* (fig. 288). The *weight* of the evolved carbonic acid is determined by accurately weighing the condenser with its alkaline solution, before and after the experiment.

When *nitrogen* is a component of the organic matter under examination, the mixture with oxide of copper is made as usual, but the contents of the fore-part of the analyzing-tube *c* (fig. 284), must now consist of a mixture of shavings or filings of metallic copper with the oxide, and great care must be taken slowly to conduct the evolved gases through this mixture, rather highly heated, in order to effect the complete evolution of the nitrogen, and to decompose the various compounds which that substance might possibly form with the oxygen, carbon, or hydrogen. The nitrogen then escapes through the tube *k*, (containing fragments of caustic potassa, or of chloride of calcium, to deprive it of humidity,) and must be collected over mercury by connecting the end of that tube with the apparatus *g*, *h*, *i*, (fig. 286.) It is, however, in general, better, in cases where the analysis is complicated by the presence of nitrogen, to make a separate experiment for the determination of its quantity: in

* This useful apparatus is the contrivance of Justus Liebig. (*Pogg. Ann.*, xxi.)

that case, the evolved gases, (carbonic acid and nitrogen,) may be collected in the mercurial apparatus, and the carbonic acid abstracted by a few fragments of fused hydrate of potassa, when the nitrogen will remain, and its weight may then be inferred from the accurate determination of its bulk.

There are some useful remarks on organic analysis in a paper by Persoz (*Ann. de Ch. et Ph.*, LXXV. 6), who employs sulphate of mercury as a substitute for oxide of copper in the combustion-tube.

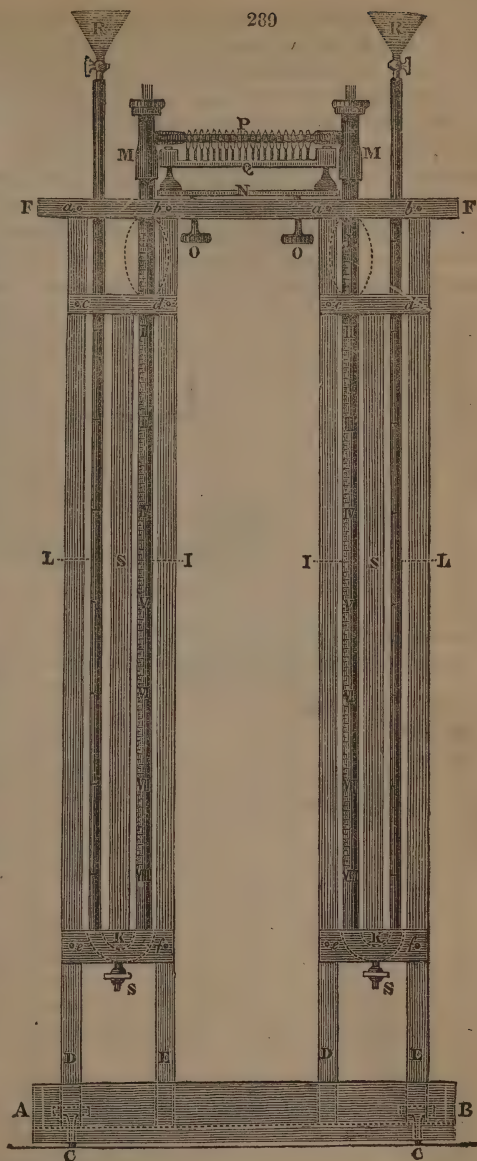
My object in the preceding details, has been to render the *principles* of the ultimate analysis of organic products intelligible to the student; the manipulations, in all their details, scarcely admit of useful description, and can only be learned by practice; and the beginner will, I think, do well to make each element the object of a separate experiment; I mean, to employ one portion of the matter under examination for the determination of the quantity of water formed, or of the elementary hydrogen; another for the determination of the quantity of carbonic acid formed, or of the elementary carbon; and another for the nitrogen. The most experienced and dexterous chemist will also require repetitions of his analyses; and in undertaking these, he will do well to follow the recommendation of Dumas, who advises that these experiments should be made upon each substance in increasing quantities; one, for instance, upon *two*, one upon *four*, and one upon *six* grains; or in some such proportions.

I shall conclude these observations upon the ultimate analysis of organic products, with the following abstract from Dr. Prout's paper upon this subject, (*Phil. Trans.*, 1827,) which will elucidate some of the points that may appear obscure in the preceding paragraphs, and further explain some manipulatory details. Dr. Prout's object was, effectually to burn the organic substance in oxygen gas; in which case, supposing it to contain three elements, hydrogen, carbon, and oxygen, one of three things happens. 1. The original bulk of the oxygen gas *remains the same*, in which case *the hydrogen and oxygen in the substance exist in it in the same proportions in which they exist in water*; or, 2. The original bulk of the oxygen is *increased*, in which case the oxygen exists in the substance in a *greater* proportion than it exists in water; or, 3. The original bulk of the oxygen is *diminished*, in which case the *hydrogen predominates*.

Hence, in the first of these cases, the composition of a substance may be determined by ascertaining the quantity of *carbonic acid gas* yielded by a known quantity of it; while in the other two, the same can be readily ascertained by the same data, and by noting the excess or diminution of the original bulk of the oxygen.

Fig. 289, represents a front view of Dr. Prout's apparatus, for the determination of these points. AB is a platform, two feet square, surrounded by a ledge for preserving any mercury that may fall about, and furnished with four adjusting screws (of two of which, c c are sectional views). Into this platform are fixed perpendicularly four pillars, DE, DE, about four feet and a half high, supporting another small platform, FF, about four inches wide, and which may be fixed or removed at pleasure by the brass pins, a b, a b. II are glass tubes, graduated to hundredths of a cubic inch, and cemented at bottom into semicircular iron tubes enclosed in

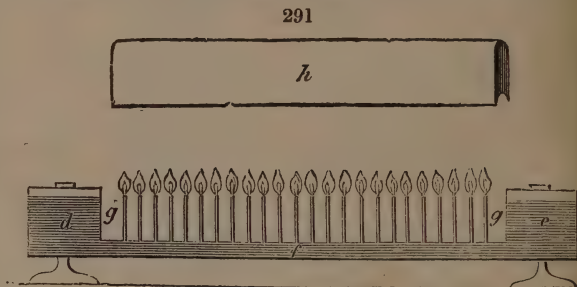
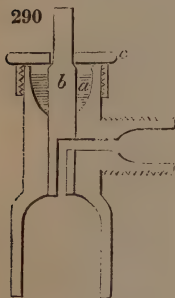
the blocks $\kappa \kappa$ (as represented by the dotted lines). These iron tubes project a little below the wood at the lower part, where they are furnished with iron stop-cocks, $s s$, for drawing off the mercury when it may be necessary. Into the other end of these semi-circular tubes are likewise cemented the glass tubes, $l l$ (of smaller dimensions, and a little longer than the tubes ii), and forming with them, when taken together, inverted siphons. The smaller tubes, $l l$, are surmounted by funnels, $r r$, furnished with stop-cocks, the object of which is to permit the mercury to flow into them with any velocity that may be required. On the tops of the larger tubes, ii , are cemented the vertical stop-cocks, $m m$, of which fig. 290 is a sectional view on a larger scale, and which renders the construction so obvious, that perhaps no further remark is necessary, than merely stating that the cup a is filled with oil, and that the plug b , which is square at the upper part, and adapted to a key, is furnished with a shoulder, on which the screw-cap, c , rests, and by means of which it may be tightened at pleasure*.



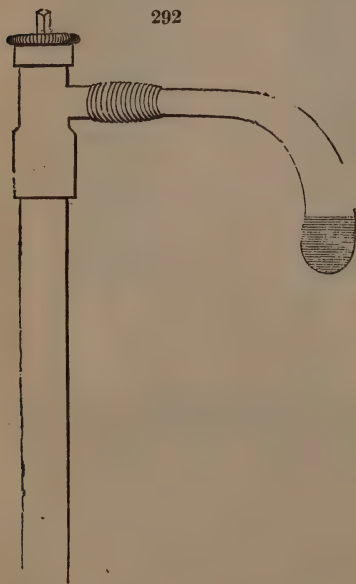
* The siphons are fixed together independently of the general frame-work, and may be removed at pleasure by taking out the pins cd , cd , and ef , ef . This admits of their being replaced by others of different sizes. Those of a larger size have balls near the top, as represented by the dotted lines, and may

contain as much as 20 cubic inches of gas. It much facilitates the process of determining the exact quantity of gas contained in the apparatus, to have both legs of the siphon graduated, which may be easily done so as to obviate the effects of capillary attraction when the tubes are not both of the same calibre.

On the platform, *FF* (fig. 289), is a thin piece of wood, *N*, capable of being raised or depressed by the screws, *oo*; on this the lamp, *Q*, is placed, at any distance that may be required from the tube *P*. Fig. 291 is an enlarged view of this lamp; it consists of two reservoirs, *de*, for holding the spirit, connected together by means of the tube, *f*, into which are placed, at the distance from one another of about $\frac{1}{3}$ of an inch, a number of vertical burners, *gg*, about one-twelfth of an inch in diameter, and $\frac{3}{4}$ of an inch long, and *made as thin* as possible, with the view of preventing the conduction of the heat. These burners are each furnished with a few threads of cotton, and are bent a little alternately like the teeth of a saw, in order that their flame may envelop the tube *P* (fig. 289)



more completely: *h* is a cover for the wick of the lamp when not in use. The tube *P* (fig. 289) is of green or bottle glass, moderately stout, and about one-fifth of an inch internal diameter. It is fixed between the horizontal parts of the vertical cocks, *MM*, so as to be perfectly air-tight; and when required, the whole, or any part of it, may be heated by means of the lamp, *Q*, at the pleasure of the operator.



When the apparatus is to be employed, both the siphon-gasometers, *IL*, *IL*, are to be filled with quicksilver, and a small green-glass retort, containing the requisite quantity of chlorate of potassa (previously heated so as to expel the common air, and fill it with oxygen) is to be attached to one of the cocks, as represented in fig. 292, by means of a caoutchouc tube. Heat is then to be applied, and any quantity of oxygen gas that may be required, introduced into the tube *I*. After the whole has acquired the temperature of the atmo-

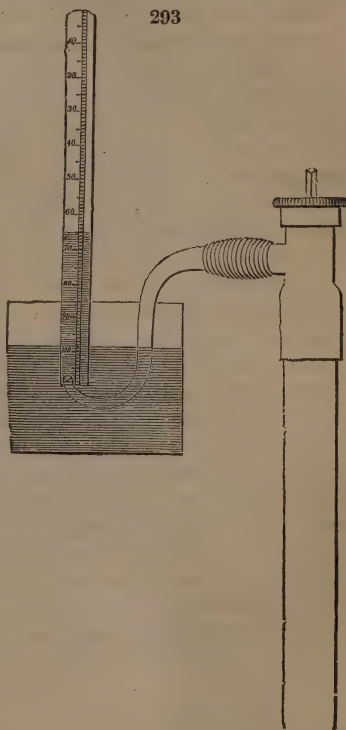
sphere, the exact quantity of the gas is to be accurately noticed, as well as the state of the barometer and thermometer at the time. The tube *P*,

containing the substance to be analyzed, is then to be firmly fixed between the cocks, *MM**, and subjected to heat, during which the oxygen gas is to be transferred from one siphon to another, through the red-hot tube, with any velocity that may be required, and which may be regulated by means of one of the stop-cocks of the funnels, *R R*, and the stop-cock, *S*, of the opposite siphon.

Such is a general view of the apparatus, and the principles of its operation; but perhaps a few practical remarks on some of the circumstances to be attended to during its employment, may not be deemed superfluous.

The substance to be analyzed may be placed in a small tray of platinum-foil, and introduced alone into the tube *P*, and gradually submitted to the action of heat and oxygen gas; but this does not answer well with organic compounds, as a portion of them is apt to escape combustion. Another method is, to mix the substance with pure siliceous sand, and to retain the mixture in the centre of the tube by means of asbestos. But this method often fails, except there be about an inch of the oxide of copper at each end of the tube, which must be kept red-hot during the experiment, and in this case it succeeds completely with many substances. Another method, and that which the most generally succeeds, is to mix the substance with oxide of copper, to heat these together in the tube, in the first place, and afterwards to open the other stop-cock and send the oxygen gas through the ignited and partially reduced oxide, by means of which

it again becomes peroxidized; and any portion of the substance that had escaped complete combustion in the first part of the experiment, is now completely burnt. This last method is also that employed when it is required to determine the quantity of carbonic acid gas yielded by a given quantity of any substance; only in this case, of course, oxygen gas is not required, and the contents of the tube *P* must be taken out and well triturated, and subjected to heat a second time. If it should be required to analyze the gas formed, one method of removing it from the tube, *I*,



* I have tried various modes of connecting the tube so as to ensure its being air-tight. Caoutchouc answers very well; but the best substance are slips of thin moistened hog's bladder, tied on

very tightly with fine *dry* twine. The twine is then to be moistened also, and the whole kept in this state till the end of the experiment.

is represented at fig. 293; and others will readily occur to the practical chemist.

The following are some of the advantages of this apparatus and mode of analyzing organic compounds. In the first and chief place, *there is nothing to be apprehended from moisture*. Whether the substance to be analyzed be naturally a hydrate, or in whatever state it may be with respect to water, the results will not be affected; and the great problem, whether the hydrogen and oxygen exist in the substance in the proportions in which they form water, or whether the hydrogen or oxygen predominates, will be equally satisfactorily solved, and that (of course within certain limits), independently of the weight of the substance operated on*. When, however, it is the object to ascertain the quantities of carbonic acid gas and water yielded by a substance, it is, of course, necessary to operate on a known weight; but this being once determined, there is no fear, as in the common methods, of exposing the substance to the atmosphere as long as may be necessary. The hygrometric properties of the oxide of copper, as well as its property of condensing air, are also completely neutralized, for the whole, at the end of the experiment, being left precisely in the same state as it was at the commencement, the same condensation of course must take place, and any little differences that may exist are rendered quite unimportant from the bulk of oxygen gas operated on, which of course should, in all instances, be considerably greater than that of the carbonic acid gas formed. Another advantage of this method is, that perfect combustion is ensured by it. There is also no trouble of collecting or estimating the quantity of water, a part of the common process attended with much trouble, and liable to innumerable accidental errors, besides those already mentioned, and which there is no method of obviating or appreciating; here, on the contrary, the results are obtained in an obvious and permanent form, and from the ease with which they are thus verified, comparatively very little subject to error.

The form and principles of this apparatus render it well adapted for many other chemical operations besides the analysis of organized substances. Such, for example, as the reduction of oxides by hydrogen, and a variety of others that will readily occur to the practical chemist.

In the course of the following pages, many instances will occur of the different modes of expressing the ultimate composition of organic bodies, depending, as the following examples will show, upon the particular view which may be taken of the secondary combinations of the elementary principles.

It is customary with many chemists to represent the oxygen and hydrogen in certain vegetable substances, by the term *water*, and hence, where these elements are in the ratio to each other of 8 to 1, and in union with carbon only, the expression *hydrate of carbon*, is sometimes applied to the compound. In the following table, which contains the results of the ultimate analyses of several organic compounds, by Gay Lussac and Thenard, the meaning of this expression will be evident, and

* It is to be observed that, throughout the experiments, great care is taken that the gases are saturated with moisture; | the errors from this cause are thus rendered definite, and are easily corrected by tables calculated for the purpose.

also of the terms, excess of hydrogen, and excess of oxygen, as applied to such ternary compounds, in which, as will be observed, nitrogen is not present.

SUBSTANCES ANALYZED.	Carbon.	Oxygen.	Hydrogen.	Or supposing the Oxygen and Hydrogen to be in the state of Water.		
				Carbon.	Water.	Excess of Oxygen.
Sugar	42.47	50.63	6.90	42.47	57.53	0
Gum Arabic . . .	42.23	50.84	6.93	42.23	57.77	0
Starch	43.55	49.68	6.77	43.55	56.45	0
Sugar of milk . .	38.825	53.834	7.341	38.825	61.175	0
Lignin of oak . .	52.53	41.78	5.69	52.52	47.47	0
„ beech	51.45	42.73	5.82	51.45	48.55	0
Mucous acid . . .	33.69	62.67	3.62	36.69	30.16	36.15
Oxalic acid . . .	26.57	70.69	2.74	33.57	22.87	50.56
Tartaric acid . .	24.05	68.32	6.63	24.05	55.24	20.71
Citric acid . . .	33.81	59.86	6.33	33.81	52.75	13.44
Acetic acid . . .	50.22	44.15	5.63	50.22	46.91	2.87
						Hydrogen in excess.
Resin (of turpent.)	75.94	13.34	10.72	75.94	15.16	8.90
Copal	76.81	10.61	12.58	76.81	12.05	11.14
Wax	81.79	5.54	12.67	81.79	6.30	11.91
Olive oil	77.21	9.43	13.36	77.21	10.71	12.08

They consider it demonstrated, in reference to these experiments, 1st. That a vegetable substance is *acid*, when the oxygen which it contains is, to the hydrogen, in a proportion greater than is necessary to form water; or where there is *excess of oxygen*. 2nd. That a vegetable substance is *resinous, oily, or alcoholic*, where the oxygen is to the hydrogen in a less proportion than in water, or where there is *excess of hydrogen*; and, 3rd. That a vegetable substance is neither acid nor resinous, but *saccharine, mucilaginous, &c.*, where the oxygen and hydrogen are in the same relative proportion as in water, or where there is *no excess of either*.

To the correctness of these results, there are, however, exceptions, some of which have been pointed out by Saussure (THOMSON'S *Annals*, vol. vi.), and by Daniell (*Journal of Science and Arts*, vi. 326); but we shall have again to refer to other analyses of the above important products. The vegetable principles, also, which include nitrogen, and among which are the *vegeto-alkaloids*, are not contained in the above table, so that, admitting the general *principle of classification*, it may be modified as follows, in reference to vegetable proximate principles:—

1. Triple compounds of carbon, hydrogen, and oxygen, in which the hydrogen and oxygen bear to each other the same relative proportion as in water, and which therefore are represented by (*car* + *q*).

2. Similar triple compounds, in which there is excess of hydrogen; or (*car* + *q* + *h*).

3. Similar triple compounds, in which there is excess of oxygen; or (*car* + *q* + *o*).

4. Quadruple compounds of the above elements, with the addition of nitrogen, and represented by $(car + h + o + n)$.

5. There are also some important organic products belonging to the class of *hydrocarbons*, which will require much of our attention, and some of which, together with their general distinctive characters, have been already adverted to in the section on Carbon. Although, therefore, it will be necessary often to digress from the arrangement of the vegetable proximate principles suggested by the above considerations, it may be resorted to as furnishing a general standard of reference.

But, the mere determination of the relative proportions of the ultimate elements of these proximate principles, is not the only difficulty which this branch of the science presents: they must be viewed in reference to the Atomic Theory, in such a way, as to ascertain what number of *elementary atoms* are probably contained in what may be termed the *proximate atom*. Let us, for instance, suppose the case of *tartaric acid*: it contains per cent. 36 carbon, 3 hydrogen, 61 oxygen, and is therefore represented in general terms by $(car + q + o)$, but how can its ultimate atomic composition be made to tally with its *proximate equivalent*? The proximate equivalent of *anhydrous tartaric acid*, deduced from the weight of it which saturates salifiable bases, is 66; if now, in reference to this equivalent, we consider it as constituted of 4 atoms of carbon, 2 of hydrogen, and 5 of oxygen, we shall obtain numbers closely corresponding with the experimental results; and which, therefore, we may presume to be the correct composition of its proximate atom. Again, in reference to *citric acid*: analysis gives us its component parts per cent. as 41.38 carbon, 3.45 hydrogen, 55.17 oxygen, and these relative proportions may be atomically represented by 2 atoms of carbon, 1 of hydrogen, and 2 of oxygen, which give the *proximate equivalent* 29. But then, *one* atom of any salifiable base, oxide of lead for instance, is neutralized, not by 29, but by 58 of citric acid; we therefore assume its elementary composition to be 4 carbon, 2 hydrogen, and 4 oxygen = 58, which number coincides with its proximate equivalent, or combining proportion.

There is another very important but difficult consideration, arising out of these views of the ultimate composition of the organic proximate principles, which relates to the different views which may be taken of the manner in which the ultimate elements are arranged, or of the state in which they exist, in the original substance, before its decomposition. These views materially affect the perspicuity of our arrangements, as the following instance will serve to show. Ether and alcohol are, like the acids just alluded to, compounds of carbon, hydrogen, and oxygen, but only in different proportions: ether is constituted per cent. of 64.87 carbon, 13.51 hydrogen, 21.62 oxygen. Alcohol consists of 52.18 carbon, 13.04 hydrogen, 34.78 oxygen; now the relative bearings of these numbers are such, as admit of *ether* being regarded as a compound of 4 atoms of carbon, 5 of hydrogen, and 1 of oxygen; and *alcohol* of 2 atoms of carbon, 3 of hydrogen, and 1 of oxygen. But here, the carbon and hydrogen, and the oxygen and hydrogen, are to each other in such proportions as to admit of our considering *ether* as a compound of 2 atoms of *bihydrocarbon* (or olefant gas), and 1 atom of *water*; and *alcohol* as

a compound of 1 atom of *bihydrocarbon*, and 1 of *water*; hence we have

$$\text{Ether} = 2(2h + 2car) + q = \text{dihydrate of bihydrocarbon.}$$

$$\text{Alcohol} = (2h + 2car) + q = \text{hydrate of bihydrocarbon.}$$

But there is another way of viewing the composition of these bodies, which consists in regarding *quadrihydrocarbon*, and not *bihydrocarbon*, as the form of hydrocarbon present in them, and then *ether* would be a compound of 1 atom of *quadrihydrocarbon* and 1 of *water*; and *alcohol*, a compound of 1 atom of *quadrihydrocarbon* and 2 of *water*. Or,

$$\text{Ether} = (4h + 4car) + q = \text{hydrate of quadrihydrocarbon.}$$

$$\text{Alcohol} = (4h + 4car) + 2q = \text{bihydrate of quadrihydrocarbon.}$$

A third view of the atomic nature of alcohol and ether is this; a hydrocarbon distinct from any of those already described, and composed of 5 atoms of hydrogen + 4 of carbon, (the *Ethule* of Berzelius,) is the basis of ether and of alcohol: *ether* is an *oxide* of such hydrocarbon, and *alcohol* a *hydrated oxide*. Or,

$$\text{Ether} = (5h + 4car) + o = \text{oxide of ethule.}$$

$$\text{Alcohol} = (5h + 4car + o) + q = \text{hydrate of ether.}$$

I might go on to show other theoretic views which may be taken of the atomic constitution of ether and alcohol, and also to apply the same mode of reasoning to the probable proximate arrangements of the ultimate elements in a variety of other organic compounds; I have selected the above as sufficient to point the student's attention to the importance of the subject, and as instances to which I shall afterwards have occasion to refer: the present state of organic chemistry does not admit of many such generalizations; such as may be safely adopted, I shall afterwards detail; many are too hypothetical to come within our limits; but the whole subject is of extreme interest, as promising to simplify the apparent confusion and complexity that prevail in reference to the relative proportions of the ultimate elements of organic products, and to enable us to group, or combine them under secondary forms, in many instances analogous to the binary arrangements of inorganic nature; and to apply to them an equally perspicuous nomenclature.

It is obvious, that by adopting any of the above definitions of ether and of alcohol, we acquire considerable facility in discussing their combinations, and mutual conversion into each other, and that the terms *hydrate* and *bihydrate* of *quadrihydrocarbon*, imply much more than the mere per centage statements of the elements: to illustrate this by a parallel case from inorganic chemistry; suppose a compound the ultimate elements of which are stated to be, per cent., 15.35 carbon, 41.05 oxygen, 7.75 hydrogen, 35.85 nitrogen; this statement will be found compatible with, 1 atom of carbon, 2 of oxygen, 3 of hydrogen, and 1 of nitrogen; but how much is this statement simplified, and how different its meaning, by so grouping the carbon and the oxygen as to represent *carbonic acid*, and the nitrogen and hydrogen to represent *ammonia*; the whole producing *carbonate of ammonia*, or,

Carbon	1	. .	6	. .	15.38	} Carbonic acid	1	. .	22	. .	56.4
Oxygen	2	. .	16	. .	41.02						
Hydrogen	3	. .	3	. .	7.69						
Nitrogen	1	. .	14	. .	35.90	} Ammonia	. 1	. .	17	. .	43.6
	1		39		100.00						
							1		39		100.0

I shall have to adduce many similar instances derived from organic analyses, amply supported by experiment and analogy; and, as already remarked, importantly elucidating and simplifying these complicated researches.

I now proceed to an enumeration of the principal *proximate elements*, or *immediate principles*, of the vegetable kingdom; to the methods of separating them from each other, and of obtaining them in their insulated states; to [an examination of their properties and uses; and to such views of their ultimate constitution as are founded upon researches carried on in reference to the preceding details. I cannot adhere strictly to the systematic arrangement above proposed, but it will constitute the foundation of the order in which they are enumerated. The immediately ensuing sections, therefore, of this chapter, will relate to those proximate principles in which the ultimate elements are so combined as to constitute *hydrates of carbon*, and I first select those which are of most common and general occurrence; I shall refer, as we proceed, to certain of their varieties or species, which belong to distinct *genera* of plants.

I am quite aware that the arrangement adopted in this portion of my book is open to many objections, but I have rather studied the convenience of the student, than endeavoured to satisfy the theorist. When Liebig's work is complete, we shall be better able to judge of its perspicuity, but as far as arrangement is concerned, the published volume does not appear to me at all calculated to aid the beginner in this difficult branch of the science: the same objections apply to the fifth volume of Dumas' valuable and elaborate treatise, which is also unfinished; indeed, some fatality seems to attend the completion of these works, arising, I presume, out of the incomplete state of many of the researches upon which the respective views of their eminent authors are essentially founded, and the difficulty of completing a stable superstructure upon either of their foundations. The nomenclature, which, among the continental chemists, is creeping into organic chemistry, cannot, I think, be too strongly protested against by all who are engaged in teaching chemistry: neither arrangement nor nomenclature are of much importance to those who have advanced far into, and are familiar with, the more complicated details of the science; but to the student, the capricious and hypothetical terms which are in vogue are either unintelligible, or what is worse, are calculated to mislead and embarrass.

§ III. GUM, MUCILAGE, AND THEIR VARIETIES. PECTIN AND PECTIC ACID. MUCIC ACID AND PYROMUCIC ACID.

UNDER the term *gum* are included several modifications of a distinct proximate principle of vegetables, which are of extremely common and almost universal occurrence. To some of these the term *mucilage* is occasionally applied; and all the varieties may be referred to one or

other of these species, *gum arabic* furnishing a characteristic specimen of GUM, and *gum tragacanth* of MUCILAGE; the former the produce of the *Acacia vera*; the latter of the *Astragalus tragacantha*.

GUM occurs in the form of an exudation upon the bark of trees, and collects into drops which gradually harden by exposure, and of which gum arabic furnishes a very perfect example: it may also be discovered, more or less abundantly, in the sap and juices of almost all plants and fruits, where it is recognised by the properties we are about to describe.

GUM ARABIC occurs in rounded pieces, or *tears*, of various sizes; and when pure is brittle, transparent, colourless, tasteless, inodorous, and of a specific gravity varying between 1.30 and 1.50. It does not crystallize, but when its aqueous solution is slowly evaporated, it remains in a hydrated state, and, though apparently dry, retains about 17 per cent. of water, which is given off by desiccation in vacuo over sulphuric acid at 212° . Heated above 212° it becomes yellowish, and slightly sour; and when subjected to destructive distillation, yields acid water, empyreumatic oil, carbonic acid, and carburetted hydrogen, and leaves a spongy residue of charcoal.

Gum is slowly soluble in cold water, and more rapidly in boiling water, yielding a mucilaginous solution, which is more or less viscid and clammy according to the proportion of gum. This solution is sometimes used as a glaze or varnish, and to give a gloss and stiffness to ribands, calico, &c. When substances, in a state of minute mechanical division, are suspended in it, it prevents their subsidence; hence its employment as an ingredient of writing-ink, and of some paints. It is quite insoluble in absolute alcohol and in ether; hence alcohol occasions a white precipitate of hydrated gum, when added to its aqueous solution.

When powdered gum arabic is triturated into a paste with *sulphuric acid*, the mixture gradually becomes brown, and if, after it has stood for 24 hours, it is diluted with water and saturated by chalk, so as to abstract the acid, the gum retained in solution is somewhat modified, and resembles that which we shall afterwards describe as produced by the action of sulphuric acid upon lignin. Heated with sulphuric acid, gum is decomposed, sulphurous acid, and traces of acetic acid, and of artificial tannin are formed, and about 30 per cent. of carbon deposited upon the addition of water. Boiled with *very dilute* sulphuric acid, it is partially converted into sugar. *Nitric acid* decomposes gum, and, when aided by heat, nitric oxide is evolved, and from 14 to 26 per cent. of mucic acid deposited on cooling. Longer digestion produces malic and oxalic acid. It would appear, from Vauquelin's experiments, that when chlorine is passed through a solution of gum, a portion of citric acid is generated, but this requires verification. Powdered gum absorbs chlorine, and becomes brown and soft; it also absorbs hydrochloric acid, becoming brown, viscid, and evolving the gas when acted on by sulphuric acid. Iodine is apparently without action upon gum.

The action of *salifiable bases*, and of *salts*, upon gum, has been inquired into by Berzelius, Pfaff, Bostock, Thomson, and several other chemists. According to Berzelius, a concentrated solution of gum is first

coagulated by caustic potassa, and then gradually liquifies; alcohol throws down from the solution a compound of gum and potassa in the form of a curdy precipitate, which, when dried, is brittle and soluble in water: similar combinations may be made with the other alkalis and alkaline earths. When recently-precipitated hydrated oxide of lead is digested in an aqueous solution of gum, a definite compound of gum and oxide of lead is formed: the same compound is obtained by adding subnitrate or subacetate of lead to a solution of gum, or by adding ammonia, not in excess, to a mixed solution of gum and nitrate of lead; it is white and insoluble, and when carefully dried consists of 61.75 gum, and 38.25 oxide of lead. A solution of *gum arabic* is precipitated by silicate of potassa; it is coagulated by a solution of borax, and the coagulum is soluble in free acid: in this respect gum resembles starch, but differs from mucilage. When persulphate of iron is dropped into solution of gum arabic, a yellow gelatinous precipitate falls, soluble in free acid and in caustic potassa, but only partially soluble in boiling water: 1 part of gum in 1000 of water gives a yellow precipitate after 24 hours. This action upon persalts of iron is peculiar to gum arabic. Protonitrate of mercury also affords a precipitate with gum. (BERZELIUS.)

The term MUCILAGE is applied to a modification of gum, of which the substance known in commerce as *gum tragacanth* may be taken as the type. It is in the form of white or yellowish semitransparent flakes, or curled and crinkled pieces, and so tough as not to admit of being powdered till dried at 212° , when it loses about 10 per cent. of water, and becomes brittle. It does not dissolve like gum arabic, but when steeped in water swells into a bulky mucilaginous mass, which, when boiled with water, gradually acquires the appearance of a solution of ordinary gum. According to Guerin, 100 parts of tragacanth yield 53 of *gum* (analogous to gum arabic), and 33 of *mucilage* (or *Bassorin*, a mucilaginous substance, described by Vauquelin as forming the bulk of gum Bassora, *Ann. du Museum*, xvi. 167), the remainder being water and oxalate of lime.

Gum Senegal, *Cherry-tree Gum* (*cerasin*), and that of *peach* and *apricot* trees, and other species of *Prunus*, together with the gum of starch and lignin, artificial products afterwards to be noticed, are closely analogous to gum arabic, or become so when they are boiled with water. The mucilage of *quince-seed*, *linseed*, of the petals of the *marigold* (GEIGER's *Calendulin*), and that of several of the gum-resins, partake of the generic characters of tragacanth, or of mixtures of gum and mucilage. *Sarcocolla* and *salep* also exhibit the same characters.

ULTIMATE COMPOSITION AND EQUIVALENT OF GUM. — According to Berzelius' analysis of the insoluble and anhydrous compound of gum and oxide of lead (gummate of lead), the oxygen in the gum is to that in the oxide of lead as 12 to 1, and if we regard it as a *neutral compound*, it will consist of

						Berzelius.
Gum	1	61.75
Oxide of lead	1	38.25
Gummate of lead	1		218	100.0		100.00

The ultimate composition of gum, therefore, as represented by Berzelius, is shown in the following table, together with the results of some other analysts (excluding a *trace* of nitrogen).

				Berzelius.	Prout.	Gay Lussac.	Berthollet.
Carbon	13	78	41.94	41.906	41.4	42.24	43.80
Hydrogen	12	12	6.45	6.788	6.5	6.93	6.86
Oxygen	12	96	51.61	51.306	52.1	50.83	49.34
Gum	1	186	100.00	100.000	100.0	100.00	100.00

PECTIN. PECTIC ACID.—Under this term (from *πηκτις*, *coagulum*), Braconnot has described the *jelly* of fruits, a substance which had generally been regarded as a compound of gum and vegetable acid: it had been distinguished from animal jelly by deficiency in nitrogen. It is obtained from many fruits, by carefully expressing their juice and evaporating it more or less, at a temperature not exceeding 212° . It may be obtained by the addition of alcohol to recently-expressed currant or gooseberry juice: in the course of a few hours a gelatinous substance separates, which must be washed with weak alcohol and dried: it then resembles isinglass in appearance, and, when digested in cold water, swells into a soft pulp like starch, but is not blued by iodine. When heated with a small quantity of potassa, or soda, or of their carbonates, it is converted into what has been termed *Pectic acid*. This acid is easily obtained by the action of alkalis on the ligneous tissue of some vegetables: it combines with bases, and may be again separated from them by other acids. (BRACNOT, *Ann. de Ch. et Ph.*, xxviii. and xxx.) The *alkaline pectates* are soluble, but the *pectate of lime* is insoluble. It may be procured from the rasped roots of carrots and turnips. Deposited from a mixture of one-fourth of the juice of cherries and three-fourths of the juice of gooseberries, and, washed carefully, first with dilute alcohol, and then with cold distilled water, it is pure, with the exception of a little colouring-matter.

To obtain pectic acid from the carrot, the root is rasped, pressed, and washed with common water, until the latter passes off limpid. Every 100 parts of the pressed carrot, with 5 parts of bicarbonate of potassa, are boiled in water to form a clear fluid, and then again pressed; a strong solution of *pectate of potassa* is thus obtained, which, being decomposed by excess of solution of chloride of calcium, gives an insoluble *pectate of lime*. This, washed, and treated with water acidulated by hydrochloric acid, and finally with pure water, affords pure *pectic acid*. In preparing it in this or any other way, water containing earthy salts should be carefully avoided, as they are decomposed, and precipitate it. It has been much recommended in France as a part of the diet of invalids, and is said to be an antidote against many of the poisonous salts. (*Ann. de Ch. et Ph.*, xxx. 96.)

Pectic acid has not been quantitatively analyzed, but pectate of potassa (neutral) is said to consist of 15 potassa + 85 pectic acid; so that the equivalent of the pectic acid would be about 270.

MUCIC ACID. SACLACTIC ACID.—This acid is produced by the action of nitric acid upon *gum*, or upon *sugar of milk*. It was discovered by Scheele. (*Opusc.*, ii. 3.) It is obtained by heating in a retort about

3 parts of gum arabic and 5 of nitric acid, diluted with half its weight of water; carbonic acid and nitrous gas are evolved, and when the effervescence has nearly ceased, the mixture is allowed to cool: it then deposits a white sediment, which is mucic acid: 1 part of *sugar of milk* may be substituted for the gum, and exactly the same product is obtained. It may be purified as follows: add ammonia, in slight excess, to the impure acid, and afterwards as much boiling distilled water as will dissolve the salt formed. Filter the solution while boiling-hot, and then evaporate it very slowly, nearly to dryness. The *mucate of ammonia* will be separated in the form of crystals, which are to be washed with cold distilled water till they become quite white and pure. They are now to be again dissolved in distilled water, and the boiling saturated solution permitted to drop from a filter into cold diluted nitric acid. This latter, of course, decomposes the mucate, and precipitates the acid in a state of purity. (PROUT, *Phil. Trans.*, 1827.) This acid is sparingly soluble in water, requiring 60 parts, at 212° , and is deposited, as the solution cools, in the form of a white gritty powder, of a slightly acid taste. It is insoluble in alcohol. It combines with the metallic oxides, and forms a class of salts called *mucates*, or *sacclactates*.

The salts of this acid have been especially examined by Trommsdorff, who, with Berzelius, agrees in assigning to it the equivalent 105: according to these chemists the *mucate of lead*, which is insoluble in water, consists of

				Berzelius.	Trommsdorff.
Oxide of lead	1	112	51.61	51.66	51.5
Mucic acid	1	105	48.39	48.34	48.5
Mucate of lead	1	217	100.00	100.00	100.0

The following are the analyses of the *mucic acid* in reference to this equivalent:—

				Berzelius.	Gay Lussac and Thenard.	Prout.
Carbon	6	36	34.29	33.430	33.69	33.33
Hydrogen	5	5	4.76	5.105	3.62	4.94
Oxygen	8	64	60.95	61.465	62.69	61.73
Mucic acid	1	105	100.00	100.000	100.00	100.00

PYROMUCIC ACID.—When mucic acid is subjected to destructive distillation it yields about one-fifteenth of its weight of *pyromucic acid*, part of which sublimes, and part dissolves in the distilled liquid. The whole is dissolved in water, and filtered through animal charcoal, evaporated and crystallized, or again sublimed. This acid is permanent in the air, inodorous, very sour, fusible at 270° , and rises in vapour at a few degrees above that point, condensing in drops which concrete in fine acicular crystals, soluble in 26 parts of cold, and in less of boiling water, and more soluble in alcohol. (HOUTON LABILLARDIÈRE, *Ann. de Ch. et Ph.*, ix. 365.) It consists, in its anhydrous or combined state, of

				Boussingault.
Carbon	10	60	58.3	58.74
Hydrogen	3	3	2.9	2.88
Oxygen	5	40	38.8	38.38
Pyromucic acid	1	103	100.0	100.00

The crystallized acid appears to include 2 atoms of water, and, according to Dumas, is isomeric with *pyrocitric acid*, and, in its anhydrous state, with the *pyromeconic*.

The salts of this acid (*Pyromucates*) are almost all soluble: the only metallic salts which are precipitated by it being those of the peroxide of iron, protoxide of mercury, and of tin. It is as good a precipitant of the persalts of iron as succinic, or benzoic acid.

PARAMUCIC ACID.—Under this term Malaguti has described an acid separable by alcohol from the mucic acid. (*Journ. de Pharm.*, xxi. 640.)

§ IV. SUGAR.

CANE SUGAR. HONEY SUGAR. GRAPE SUGAR. MANNITE. LIQUORICE SUGAR, OR GLYCYRHIZIN. MUSHROOM SUGAR.

SUGAR may be extracted from the juice of a number of vegetables, and is contained in all those having a *sweet* taste: that which is commonly employed is the produce of the *Arundo saccharifera*, or *sugar-cane*, a plant which thrives in hot climates.

The constituents of *cane-juice* are

Water,	Albumen,	Acetate of Lime,
Sugar,	Green Fecula,	Acetate of Potash,
Gum,	Lignin,	Super Malate of
Mucilage,	Acetic Acid,	Lime,
Gluten,	Malic Acid,	Sulphate of Lime.

CRYSTALLIZABLE or CANE SUGAR.—The manufacture of sugar consists in isolating the concrete sugar from the substances with which it is associated in cane-juice, which is effected as follows.

The cane, when ripe, is cut off at the root, stripped of leaves and ends, then passed twice through the mill, so as to express the juice. To prevent fermentation, a portion of lime (about 1 to 1600) is immediately mixed with the juice, which is then passed through a series of boilers to the last evaporating vessel called a *teache*. The syrup there is boiled until it granulates to *proof*, and is then transferred into coolers for the crystals to form and separate from the molasses or treacle; after which it is packed into hogsheads for exportation to this country, under the name of *muscovado* or *raw sugar*. During this process, the saccharine matter is affected, its colour is darkened, and its power of crystallization weakened.

It is said that when the sugar-cane has attained its full maturity for grinding, little or no colouring matter is contained in the juice, but it exists in the waxy or resinous particles combined with the green fecula, and left in the sugar, when this fecula is precipitated by the lime. During boiling, the alkali renders the colouring matter soluble, and thus, by the application of heat, the colour of the sugar is always more or less deteriorated.

By evaporating the cane-juice in open pans, the heat of the vessel

itself is above 300° Fahr., and as the juice cannot support a temperature of 225° without decomposition of the green fecula and other vegetable matter, the saccharine matter must necessarily undergo other changes. Solid *anhydrous sugar* is made fluid at 300° , and at 302° is decomposed: the syrups are therefore further darkened by the charring or carbonization at the bottom of the evaporating vessels. The saccharine matter thus decomposed is probably converted into gum. (Dr. Thomson describes sugar as differing from gum merely by containing an atom of water less. Hence an atom of sugar + an atom of water, constitute an atom of gum.)

In addition to the injurious effects of heat on the saccharine matter itself, there is another principle, opposed to crystallization, existing in the defecated juice, which is mucilage, and which, at a boiling temperature, is converted into a matter analogous to gum. As regards the *treacle*, Dr. Turner observes that "its saccharine principle has been supposed to be different from crystallizable sugar; but it consists chiefly of common sugar, which is prevented from crystallizing by the presence of foreign substances, such as saline and other vegetable matters."

The process of *Refining Sugar* consists in separating the pure crystals from the uncrystallizable and colouring matter existing in the original juice, and subsequently increased on converting this juice into *muscovado sugar*. The following is a sketch of the old process by which sugar is refined.

Raw sugar is chosen for the purpose of refining by the sharpness and brightness of the grain, and those kinds are preferred which have a peculiar gray hue. Soft-grained yellow sugars, although whiter, are not so fit for refining, and it is for this reason that sugars from particular colonies are seldom used, such as those from the East Indies, Barbadoes, &c.

The proper sugar being selected, the *pans* are charged with a certain portion of lime-water, with which bullocks' blood is well mixed by agitation. They are then filled with the sugar, which is suffered to stand a night to dissolve. The use of the lime-water is to render the molasses more soluble, and thus to facilitate its separation from the pure solid sugar. In the purer kinds, and more especially when the refined is redissolved for the purpose of bringing it to its utmost degree of purity, lime is not used; the quantity of molasses being so small as to be easily removed by the agency of water alone.

Fires are lighted under the pans early in the morning, and when the liquid begins to boil, the albumen of the blood coagulates and rises to the top, bringing the impurities of the sugar with it. These are taken off with a skimmer. The liquid is kept gently simmering and continually skimmed, till a small quantity, taken in a metallic spoon, appears transparent: this generally takes from four to five hours. The whiteness of the sugar is not improved by this process, but even sometimes deteriorated, from the action of the fire; it only serves to remove foreign impurities.

The *colour* (as the refiners term it) or *whiteness* of the sugar when refined, depends in a great measure on the quantity of animal charcoal used in this part of the process. It is applied frequently to the first

solution of the sugar and water. In some refining-houses the solution is filtered through beds of animal charcoal. The solution is, when perfectly bright and clear, run off into a large cistern.

The pans are then reduced to half their size by taking off their fronts, and a quantity of syrup returned into each, which is made to boil as rapidly as possible, till it is capable of being drawn into threads. Nothing but practice can ascertain the exact point at which the boiling should be stopped: if carried too far, the molasses is again bound up with the sugar; and if not carried far enough, much of the sugar runs off with the molasses in the after-process. When this point is ascertained, the fire is damped, and the boiling sugar carried to the *coolers*: a fresh quantity is then pumped into the pans, which is evaporated as before.

When the sugar is in the coolers, it is agitated with wooden oars till it appears granulated, and is no longer capable of being drawn into threads. It is upon this agitation in the cooler that the whiteness and fineness of grain in the refined sugar depend. The crystals are thus broken whilst forming, and the whole converted into a granular mass, which permits the coloured liquid saccharine matter to run off, and which would be combined with the solid, if suffered to form in larger crystals. This granular texture likewise facilitates the percolation of water through the loaves in the after-process, which washes the minutely-divided crystals from all remaining molasses. That this is the true theory of the whitening of sugar by the process of refining, appears from a comparison with the process of making *candy*. In this latter, the raw material is cleared and boiled exactly in the same manner; but instead of being put into coolers and agitated, it is poured into pots, across which threads are strung, to which the crystals attach themselves; these are set in a stove, and great care is taken not to disturb the liquid, as upon this depends the largeness and beauty of the candy. In this state it is left for five or six days, exposed to a heat of about 95° , when it is taken out and washed with lime-water: this takes off the molasses from the outside, but a portion is combined in the crystals, and the consequence is, that candy is never whiter than the sugar from which it is made.

When the sugar has arrived at that granular state in the coolers, above described, it is poured into conical earthen moulds, which have previously been soaked a night in water. In these it is again agitated with sticks, for the purpose of extricating the air-bubbles which would otherwise adhere to the sugar and the moulds, and leave the coat of the loaf rough and uneven. When sufficiently cold, the moulds are taken to the upper floors of the manufactory, and the paper stops being removed from their points, they are set, with their broad ends upward, upon earthen pots. The first portions of the liquid molasses soon run down, and leave the sugar whitened by the separation. This self-clearance is assisted by a high temperature; and when it is perfected, pipe-clay, carefully mixed with water to the consistence of cream, is put upon the base of the loaves to the thickness of about an inch: the water from this slowly percolates them; and, washing the solid sugar from all tinge of molasses, runs into the pots. The clay is of no other use than to retain the water, and prevent its running too rapidly through the mass,

by which too much of the sugar would be dissolved; a sponge, dipped into water, acts in the same manner. The process of *claying* is repeated four or five times, according to the nature of the sugar, and the degree to which it has been boiled. When the loaves are cleansed from all remains of the coloured fluid, they are suffered to remain some time for the water to drain off; when this is completed, they are set with their bases downwards, when all remains of it return from their points, and it is equally diffused throughout: they are then set in a stove, heated to about 95° , and thoroughly dried.

The *syrup*, or the mixed solution of sugar and molasses which runs into the pots, is mingled in the next boilings with the solution of raw sugar in the pans, and again evaporated. It is divided according to its fineness; the first running, containing most molasses, is reserved for the coarser loaves; whilst the last, being little else than a solution of sugar, is boiled into loaves, of the same degree of fineness as those from which it ran. The lowest syrups are boiled into what is called *bastard sugar*, from which the molasses runs with very little mixture of the solid sugar. This is called *treacle*, and is incapable of further crystallization.

The produce of 1 cwt. of raw sugar worked in this manner is, upon an average, 63 lbs. refined, 18 lbs. bastard, 27 lbs. molasses, 4 lbs. lost weight, dirt, &c.

The process above described may almost be considered as mechanical. The only truly chemical parts of it are the clearing with blood, and the use of lime-water, which combines with the molasses, and facilitates its solution during the percolation of the water.

It cannot be doubted that much improvement may be made in *refining sugar*, by the aid of chemistry, so as to produce a larger quantity of *refined* from *raw sugar*, by extracting all the foreign matters remaining in the raw sugar, and which, when again exposed to high temperatures, in the process of refining, further decompose the saccharine matter. The plan of refining by open pans is now nearly superseded in this country, by the application of steam, and Howard's plan of evaporating *in vacuo*, or at least under a greatly-diminished atmospheric pressure, by which, exposure to any temperature liable to injure the sugar, is effectually prevented. The process of *claying* is also now generally omitted, and a strong solution of very white sugar is substituted, upon the principle that water, having a stronger affinity for the molasses than for the solid sugar, will, in percolating the crystals, dissolve the molasses, and leave the sugar to enlarge and aggregate the crystals, rendering the *loaves* of more weight and closer grain.

In the boiling of sugar it is obviously desirable to avoid such elevation of temperature as may in any way tend to discolour or decompose it, and high-pressure steam, oil, and various saline solutions, have accordingly been resorted to as media for the communication of heat, the object being rapidly to boil and evaporate, without elevating the temperature to that point at which sugar suffers incipient decomposition. According to Dr. Henry, "a mixture of 1 part of water and 3 of sugar boils rapidly at 230° ; and from this to 240° is its due temperature. If a solution of sugar be further concentrated by the evaporation of water, the thermometer rises to 340° . The sugar then begins to turn black, and

at 370° it takes fire, on applying flame to its vapour, and burns strongly, leaving a residuum of charcoal."

CANE SUGAR is a white brittle substance of a pure sweet taste. Its specific gravity is about 1.5 to 1.6. It is dissolved in its own weight of cold water, and boiling water dissolves a considerably larger quantity. This aqueous solution is called *syrup*; it is viscid, and furnishes crystals in the form of four and six-sided prisms, irregularly terminated, composed, according to Berzelius, of 100 sugar + 5.6 water. When syrup is long kept at a temperature near its boiling point, it loses the property of crystallizing. Sugar is soluble in alcohol, but more sparingly so than in water; when of the specific gravity of .830, it takes up about one-fourth its weight of pure white sugar; but absolute alcohol dissolves only about one-eightieth of its weight at its boiling-point, and on cooling, almost the whole separates in small crystals. When equal parts of strong syrup and alcohol are mixed, a quantity of small brilliant crystals of sugar are soon deposited.

Pure sugar is unchanged by air, and perfectly-pure syrup is not prone to change; but the addition of other vegetable substances, though in very minute quantity, materially influences the action of air on this solution. These, and other changes of such mixtures, we shall consider under the article *Fermentation*.

Concentrated sulphuric acid decomposes sugar, evolving charcoal, and producing water and formic acid. It is a striking experiment to mix about equal bulks of strong syrup and sulphuric acid; the mixture, when stirred, presently becomes brown and black, then suddenly heats, effervesces, and passes into the state of an almost solid and very bulky magma of charcoal: the acid appears suddenly to abstract from the sugar the elements of water.

When sugar is dissolved in dilute sulphuric acid and long boiled, it is gradually altered and converted into that modification of sugar which is obtained by the action of the same acid upon starch. Nitric acid converts sugar into oxalic and other acids. (See *Oxalic Acid*.) Chlorine and hydrochloric acid gas are absorbed by sugar; they render it brown and clammy; and chlorine yields hydrochloric acid, and apparently some malic acid. If the chlorine and sugar are both dry, there is no action. (LIEBIG.) When 3 or 4 per cent. of oxalic or tartaric acid are added to sugar, it is rendered permanently uncrystallizable; other vegetable acids produce a similar effect, and the uncrystallizability of molasses is partly referable to a similar cause.

Arsenic acid renders syrup pink, purple, and brown, and the odour of acetic acid is evolved. When the arsenic acid is decomposed by sulphuretted hydrogen, a yellow sweet liquid remains, not precipitated by acetate of lead.

Sugar combines with the salifiable bases. The alkalis dissolve it, and destroy its sweet taste, which re-appears if an acid be added. When, however, they are left long in contact of sugar, they effect a more important change, becoming carbonated, and apparently converting the sugar into *gum*. (See LIEBIG, *Chimie Organique*, in reference to the theory of these changes, and the production of *melassic* and *glucic* acids.)

Sugar absorbs ammoniacal gas, and forms with it, according to Berzelius, a definite compound of 1 atom of sugar, and 1 of ammonia, but which, exposed to air, loses ammonia and leaves unaltered sugar. The hydrated alkaline earths are soluble in large proportion in syrup. When the solutions are evaporated, uncrystallizable gum-like compounds remain, insoluble in alcohol. From a solution of sugar and lime, Mr. Daniell obtained crystals of carbonate of lime and a portion of gum. The addition of phosphuret of lime to syrup produces an analogous change. (*Journal of Science and the Arts*, vi. 32.) Alcohol added to the solution of lime with excess of sugar throws down a compound of 1 atom of lime + 1 of sugar. According to Braconnot, the protracted action of lime on sugar tends to the production of carbonic, oxalic, malic, and acetic acids. (*Ann. de Ch. et Ph.*, lxxviii. 337.)

Saccharate of lime, and of baryta, and some other combinations of sugar, have been described by E. Peligot. (*Ann. de Ch. et Ph.*, lxxvii. 113.) When a solution of 4 parts of sugar and 1 of chloride of sodium is evaporated to a syrup, and left to spontaneous evaporation in a dry atmosphere, it at first deposits sugar candy, and afterwards crystals, composed of definite proportions of sugar and salt. An analogous compound of diabetic sugar had been long observed. The compound is represented by the formula $2(12\text{car} + 9\text{h} + 9\text{o}) + (30 + \text{c}) + 3\text{q}$.

Syrup dissolves hydrated oxide of copper, and the carbonate and subacetate of copper, and forms blue or green solutions, from which alkalis do not throw down the oxide, but which are decomposed by sulphuretted hydrogen and by ferrocyanuret of potassium. Some of the cupreous salts are reduced, or afford precipitated suboxide, when boiled with sugar.

When hydrated oxide of lead is digested in a solution of sugar, it forms a yellow alkaline liquid, which, on evaporation, yields a tough deliquescent mass; but when a solution of sugar is boiled with excess of the oxide, and filtered whilst hot, it deposits, after some hours, bulky flakes of an insoluble tasteless compound, which may be dried without decomposition, in vacuo: it is soluble in the acids, and when diffused through water may be decomposed by a current of carbonic acid, which forms carbonate of lead, and the sugar is evolved. Berzelius considers this as a compound of 1 atom of sugar, and 2 atoms of oxide of lead: it consists of 42.35 sugar, and 57.65 oxide of lead. Peligot obtained 59 per cent. of oxide of lead, and the other elements, in proportions corresponding to the formula $(12\text{car} + 9\text{h} + 9\text{o}) + 2(\text{pl} + \text{o})$.

When sugar is boiled with solution of nitrate of silver, a black powder is formed, which has not been examined: from perchloride of mercury it throws down the protochloride; and when mixed with solutions of peroxide of iron, the whole of the oxide cannot be precipitated by ammonia.

When sugar is exposed to a heat of 212° it undergoes no other change than that occasioned by the loss of adhering water; but at 300° it begins to fuse, becomes brown or black, evolves a little water, and is called, in this state, *caramel*; it is resolved at higher temperatures into new arrangements of its component elements. Dr. Prout found that sugar, exposed for seven hours to a temperature of 300° , only lost 0.6 per cent.

of its weight, but its properties were permanently injured. If suddenly elevated to a temperature of about 500° , it bursts into flame. The action of high temperatures upon sugar has been described by M. E. Peligot, at the end of his paper on *The Nature and Chemical Properties of Sugar*. He states that when sugar is heated in an oil-bath to 410° or 420° , it becomes dark-coloured without evolving any gaseous products, but gives off water slightly tainted with acetic acid and oil; when this has ceased, the residue is black and brilliant but perfectly soluble in water, yielding a dark solution; it is insipid and of uniform composition, consisting of

Carbon	12	. .	72	. .	47
Hydrogen	9	. .	9	. .	6
Oxygen	9	. .	72	. .	47
<hr/>					
Anhydrous sugar, or Caramel	1		153		100

In sugar, as in gum, the oxygen and hydrogen are to each other in the same relative proportions as in water, so that its ultimate composition is theoretically represented by $car + q$. But the relation of the carbon to the water, or the absolute equivalent of sugar, is not so easily determined, in consequence of the varieties of sugar differing a little in the relative proportion of carbon which they contain; if this be assumed at 40 per cent. then the carbon and water will be in the ratio of their respective equivalents, but there is, in the greater number of the analyses, an excess of carbon in reference to their equivalents, and in regard to the weight of the *proximate equivalent* of sugar, the only compound from which it can be deduced is that with oxide of lead. If the insoluble *saccharate of lead*, above described, be regarded as composed of anhydrous sugar, water, and oxide of lead, we may adopt the following statement of its atomic composition.

					Berzelius.
Anhydrous sugar	1	. .	153	. .	39.6
Water	1	. .	9	. .	2.3
Oxide of lead . . .	2	. .	224	. .	58.1
<hr/>					
Saccharate of lead	1		386		100.0

The composition of *crystallized sugar*, consistently with the analysis of Berzelius, will be

					Berzelius.
Anhydrous sugar .	1	. .	153	. .	94.74
Water	2	. .	18	. .	5.26
<hr/>					
Crystals of sugar	1		171		100.00

Or, in reference to *ultimate constituents*, crystallized sugar contains

				Berzelius.	Gay Lussac					
				Berzelius.	and Thenard.	Dobereiner.	Crum.	Berthollet.	Ure.	
Carbon . .	12	. 72	. 42.1	. 42.225	. 42.47	. 40.14	. 41.8	. 41.26	. 43.38	
Hydrogen .	11	. 11	. 6.4	. 6.600	. 6.90	. 7.05	. 6.5	. 6.97	. 6.28	
Oxygen . .	11	. 88	. 51.5	. 51.175	. 50.63	. 52.81	. 51.7	. 51.77	. 50.33	
<hr/>										
Crystallized } sugar }	1	171	100.0	100.000	100.00	100.00	100.0	100.00	100.00	

It will be observed that Peligot's analysis of caramel is, in fact, that of anhydrous sugar: hence Liebig also represents crystallized cane sugar by the formula $(12\text{car} + 9\text{h} + 9\text{o}) + 2\text{q}$. Döbereiner regards crystallized sugar as a compound of 6 atoms of carbon, 6 of hydrogen, and 6 of oxygen, the carbon being equally divided between the hydrogen and oxygen, so as to form a *carbonate of hydrocarbon*.

The following are Dr. Prout's analyses of several varieties of sugar*, designated as below.

	A	BC	D	E	FG	H
Carbon .	42·85 ..	42·00 ..	41·90 ..	42·20 ..	42·10 ..	40·88
Hydrogen .	6·35 ..	6·44 ..	6·46 ..	6·42 ..	6·43 ..	6·57
Oxygen .	50·89 ..	51·56 ..	51·64 ..	51·38 ..	51·47 ..	52·55
	100·00	100·00	100·00	100·00	100·00	100·00

A Purified candy; B West India candy; c English refined; d East India candy; e East India refined; f Maple sugar; g Beet sugar; h East India moist.

* The following is Dr. Prout's statement of the composition of the different grades of sugar. (*Phil. Trans.*, 1827.)

	Carbon.	Water.
Pure sugar-candy	42·85	57·15
Impure sugar-candy	41·5 to 42·5	58·5 to 57·5
East India sugar-candy (v)	41·9	58·1
English refined sugar	41·5 to 42·5	58·5 to 57·5
East India refined sugar (v)	42·2	57·8
Maple sugar (v)	42·1	57·9
Beet-root sugar (v)	42·1	57·9
East India moist sugar (v)	40·88	59·12
Sugar of diabetic urine	36 to 40?	64 to 60?
Sugar of Narbonne honey	36·36	63·63
Sugar from starch	36·2	63·8

[In these results *fixed* bodies only have been allowed for, and those marked (v), as occurring in commerce, are probably subject to slight variations in their composition.]

On these Dr. Prout makes the following remarks: "The *sugar-candies* of the shops frequently contain minute quantities of foreign fixed bodies, such as lime, &c., as well as others of a destructible character. Both the specimens of *India sugar-candy* I examined were obviously impure to the eye, being of a brown colour, and deliquescent; they contained, among other things, traces of potash. The *East India refined sugar* was perfectly white, but rather soft and friable, and it did not possess the fine and brilliant grain of the best refined sugars of commerce. For a specimen of the *maple sugar* I was indebted to Mr. Faraday; this, when I received it, was very impure and deliquescent, but by treating it by the process above alluded to (see *Phil. Trans.*), a

portion was separated that differed but little in its appearance from cane sugar. The *beet-root sugar* was made and refined in France; it was perfectly white, but rather soft and fine in the grain. The *East India moist sugar* was of a very low kind, and known in commerce by the name of *Burdwan sugar*; it was deprived of its hygrometric moisture before analysis by exposure to sulphuric acid under a receiver. The *diabetic sugar* was prepared as above; the results given were obtained many years ago, and I have had no opportunity of repeating the analysis with the present apparatus; I believe, however, that diabetic sugars, in general, belong to the honey variety. The *sugar of starch* was prepared by myself in the usual manner."

MAPLE SUGAR is the produce of the *Acer saccharinum*, which is cultivated as a source of sugar in North America. A hole is bored through the bark in spring, from which the sap flows to such an extent, that a tree of average size yields about 50 quarts in 24 hours; it contains 5 per cent. of sugar. The sap is collected during 5 or 6 weeks: it is rapidly boiled down, and yields a coarse sugar, which, however, may be purified by the same processes as cane sugar, and resembles it in its properties.

BEET SUGAR is obtained from the *Beta vulgaris*. The manufacture of sugar from beet-root has been successfully and extensively pursued in France: many interesting details respecting it will be found in a paper in the *Quarterly Journal*, xxi. 252. The roots, having been softened in water, are sliced, and the juice is expressed and boiled down to about two-thirds its bulk, with the addition of a little lime; it is then strained, again evaporated, and purified in the same way as cane sugar. 100 lbs. of the root furnish between 4 and 5 lbs. of purified white sugar, besides a quantity of syrup, at the average expense (in France) of between threepence and fourpence a pound.

GRANULAR SUGAR.—This modification of sugar, (the Krümel-zucker of the German chemists,) exists in the juice of several fruits, and may be produced artificially from lignin, starch, and some other substances which we shall afterwards describe: it may also be obtained from honey: it forms the saccharine concretions found in raisins; and as it exists abundantly in the juice of the *grape* it is often termed *grape sugar*. In good seasons the expressed juice of grapes contains from 30 to 40 per cent. of solid matter, the greater part of which is sugar: there is a small relative quantity of gum, extractive, gluten, and bitartrate of potassa. To obtain the sugar, the juice is neutralized by the addition of chalk or powdered marble, strained or filtered, mixed with a little white of egg, boiled, skimmed, and evaporated till of the specific gravity of 1.32. It is then allowed to cool, and in a few days it concretes into a solid mass, which is drained, and then dried by pressure: it affords about 3 parts of dry sugar and 1 of syrup. The sugar may be rendered white by boiling it with charcoal.

HONEY.—The substance secreted in the nectaries of flowers is collected by bees, and by them converted into honey and wax; the portion of sugar not required for nutriment is returned by the insect into the combs, in the form of a yellow syrup, the taste and smell of which differ a little, according to the flowers whence it has been derived, but which is always yellow, viscid, and very sweet. Honey contains two kinds of sugar; the one resembles that from the grape, the other is uncrystallizable: honey also contains a yellow colouring-matter, wax, gum, and sometimes manna sugar. The solid sugar is most easily obtained from the granular or crystalline honey, by the action of strong alcohol, which dissolves the other ingredients, but leaves the granular sugar. It may be whitened by dissolving it in water, filtering, boiling with charcoal, and evaporating the solution till it granulates when cold.

GRAPE SUGAR is less soluble in water than cane sugar, and the syrup which it affords is less viscid. It does not sweeten so effectively as cane

sugar, and is more soluble in alcohol. It is deposited from its boiling alcoholic solution in crystalline grains, which retain alcohol in combination. Many of the acids act upon it as on cane sugar, but sulphuric acid, instead of charring and decomposing it, combines with it to form a new acid (*sulphosaccharic acid**), which is not precipitable by baryta. Acids act upon it as on cane sugar, but it has less affinity for salifiable bases; it combines readily with subacetate of copper; when its solution is mixed with common salt, dodecaëdral crystals may be obtained from it, consisting of 25 chloride of sodium, 75 sugar, and about 7 per cent. of water. Dry grape and honey sugar have been analyzed with the following results.

				Grape Sugar. Saussure.	Honey Sugar. Prout.
Carbon	12	72	36.36	36.71	36.36
Hydrogen	14	14	7.07	6.78	7.07
Oxygen	14	112	56.57	56.51	56.56
	1	298	100.00	100.00	99.99

The *sugar of malted grain*, of *diabetic urine*, and that formed artificially from *starch* and from *woody fibre*, has the general characters of grape sugar: these we shall afterwards examine. A similar sugar has also been obtained from the Spanish chesnut, to the amount of about 14 per cent. from those grown in Tuscany: the French chesnuts are less saccharine.

MANNITE. MANNA SUGAR.—This species of sugar is most abundant in Manna, but is also found in beet-root, celery, asparagus, onions, and probably in many other sweet plants: it is also contained in the sap of the *larch* (and other species of *pinus*), and exudes from their bark, but it always tastes of turpentine. (*Manna Brigantina*.) Manna exudes from several species of *ash*, especially from the *Fraxinus ornus*, and *rotundifolia*. The best *flake-manna* is imported from Sicily and Calabria; it is of a buff-colour, light, and translucent. It has a slight odour, and a sweet, somewhat nauseous taste. Mannite is obtained from manna, by boiling it in alcohol: as the solution cools, it crystallizes: it may be purified by pressure. By very slow crystallization it furnishes delicate four-sided acicular prisms. It forms about four-fifths of the best manna; the residue is common sugar, and a peculiar yellowish extractive matter, in which the aperient quality of the manna resides.

Mannite is white, or nearly so, and very soluble in water: its aqueous solution, when sufficiently concentrated, concretes. Even when much diluted, it does not ferment; so that it may in this way be separated from the other varieties of sugar, for, when mixed with them, it remains undecomposed, whilst they are converted into alcohol.

The ultimate composition of mannite has not been satisfactorily

* Peligot prepared sulphosaccharic acid by carefully adding 3 parts of sulphuric acid to 1 of grape sugar fused on a water-bath: the product was dissolved in water, and saturated with carbonate of baryta, by which sulphate and sulphosaccharate of baryta were formed; the latter remains in solution. When

subacetate of lead is added to this solution, sulphosaccharate of lead falls, at first yellow, afterwards white. This, decomposed by sulphuretted hydrogen, yields a sweet slightly acid liquid, which forms soluble salts with nearly all bases: when evaporated, even in vacuo, it is resolved into sugar and sulphuric acid.

determined, in consequence of the difficulty of ascertaining whether it does or does not contain chemically-combined water; nor is there any combination of it from which its proximate equivalent can be deduced. Gmelin gives the following view of its supposed atomic constitution.

	According to Prout.				According to Saussure.			
Carbon . .	15	90	38.46	7	42	48.27		
Hydrogen . .	16	16	6.84	5	5	5.75		
Oxygen . .	16	128	54.70	5	40	45.98		
Dried at 212°	1	234	100.00	1	87	100.00		

LIQUORICE SUGAR. GLYCYRHIZIN.—When a strong infusion of liquorice-root is slowly evaporated to a small bulk, and sulphuric acid added, a precipitate falls, containing sugar and albumen, which is to be washed with water acidulated by sulphuric acid, then with pure water, and afterwards digested in alcohol, which leaves the albumen. A solution of carbonate of potassa is then dropped into the alcoholic solution till its acid is neutralized; it is filtered and evaporated, and the sugar remains in the form of a yellow transparent mass, intensely sweet, and easily soluble in alcohol and water: it is characterized by its tendency to combine with acids, bases, and salts. With acids it forms difficultly-soluble compounds. *Sulphate of glycyrrhizin* is tough, and sweet without acidity; it dissolves in boiling water, and gelatinizes on cooling: its alcoholic solution is not precipitated by water. *Acetate of glycyrrhizin* resembles the sulphate, but is more soluble, and forms a stiffer jelly. Glycyrrhizin combines with bases, and, when digested with alkaline carbonates, gradually displaces carbonic acid, and forms soluble compounds, which are not decomposed by carbonic acid. It occasions precipitates in most metallic salts. An analogous sugar has been found in the leaves of the *Abrus precatorius*, and in the root of the *Polypodium vulgare*. (BERZELIUS.)

MUSHROOM SUGAR was discovered by Braconnot in several species of *agaricus*, and other *fungi*, and by Schrader in *morels*. (*Helvella mitra*.) It is obtained by triturating the fungus with a little water, pressing it, and evaporating the expressed liquid nearly to dryness: the dry residue is digested in alcohol, and the solution yields crystals of the sugar on evaporation; they are square prisms, colourless when pure, slightly sweet, and less soluble than cane sugar. Concentrated sulphuric acid forms with it a red solution, from which a white coagulum separates on the addition of water.

§ V. STARCH AND ITS VARIETIES. INULIN. LICHENIN, ETC.

STARCH, or *Fecula*, may be separated from a variety of vegetable substances; it is contained in the esculent *grains* and other *seeds*, in many *roots*, in the *stems* of several species of *palms*, (seldom in those of dicotyledonous plants,) and in different *lichens*. The process for obtaining it consists in diffusing the powdered or bruised grain or seed, or the rasped root or stem, in cold water, which becomes white and turbid; the grosser parts may be separated by a strainer, and the milky liquor which passes

deposits the starch, which is to be washed in cold water, and dried in a gentle heat.

COMMON STARCH may be obtained by steeping the grain containing it in water till it becomes soft; then putting it into coarse linen bags, and pressing them in vats of water: a milky juice exudes, and the starch falls to the bottom of the vat. The supernatant liquor undergoes a slight fermentation, and a portion of alcohol and acetic acid are formed, which dissolve some impurities in the deposited starch; it is then collected, washed, and dried in a moderate heat. The greater part of the starch employed in this country is made in or near London. It may be obtained from the meal or flour of wheat, rye, or other grain, or from potatoes*, and other farinaceous roots, but the starch commonly sold is almost exclusively made from *wheat meal*. The process consists in disengaging the fecula and other parts of the grain from the gluten, by fermentation and repeated washing. The wheat, coarsely ground, is put into a vat with a sufficient quantity of cold water, in which it lies and ferments, sometimes seven or eight days, and at others longer, according as it may be wanted, or as the weather promotes or retards fermentation. When the fermentation is over, which is known by the starch settling at the bottom of the vat, the whole is taken out by small quantities at a time, and put into hair-sieves and washed with water, which separates the bran from it, the fine parts running through the sieve with the water into shallow tubs, or vessels, called *frames*. The fermentation becomes acetous, and what runs through the sieves contains the starch suspended in a very foul acid liquor, called *sour water*. In about two days after this operation, the starch settles at the bottom of the frames, the sour water is then drawn off, and the dirty discoloured part, which is the last that subsides, and therefore is at the top, is scraped off; the surface of the remaining starch is then washed, till it is nearly free from the mucilaginous sediment. The top, called *slimes*, is put into another frame or tub, and treated similarly, to obtain the starch from it. The starch is stirred with fresh water and strained through a finer sieve into another frame or tub, when,

* *Potato starch* is obtained by reducing potato to a pulp, and washing it with cold water upon a sieve; the fecula is deposited in the form of a white powder, denser than common starch, and exhibiting larger spherules under the microscope, but possessed of its essential characters. According to Dr. Pearson (*Repertory of Arts*, iii. 383), 100 parts of fresh potato, deprived of skin, contain water 68 to 72, and meal 32 to 28. The meal consists of starch 15 to 17, fibrous matter 8 to 9, mucilage 5 to 6.

Lampadius has also analyzed several varieties of the potato. (*Ann. Phil.* v. 39.)

Sago, *Tapioca*, and *Cassava*, are also varieties of starch. *Sago* is produced, not from the *Cycas circinalis*, nor indeed from any species of *Cycas*, but from true palms of the genus *Sagus*, and of at least

two species, the *Sagus genuina* (Rumphius), and *Sagus farinifera* (Lamarck). See HOOKER and HAMILTON, in *Curtis's Botanical Magazine*, vol. LX., or N.S., vol. ii., Plates 2826, 2867.

The *pith* of these palms is mixed with cold water, and the starchy deposit granulated and dried; its colour depends upon the heat at which it has been desiccated. Though sago possesses the leading character of starch, that of precipitating iodine blue, it differs from common starch by its solubility in cold water. (CAVENTOU.)

Tapioca and *Cassava* are prepared from an American plant, the *Iatropa manihot*, the milky juice of which is poisonous, but diffused through water deposits a harmless starch, nearly allied to sago.

being nearly cleansed of its impurities, it is called a *green water*. In two or three days the starch settles at the bottom of the frame or tub, where it is kept till it is either washed again or *boxed*. If it is washed again, in the manner above described, the part washed off is called a *white water*, instead of a *slime*; the other part being still called a *green water*. The starch, being sufficiently pure and settled, is taken out of the frames or tubs, and put into oblong boxes, about five feet long and one broad, with holes in the bottom and lined with linen cloth, to drain and harden, where it soon becomes solid enough to be cut into square lumps: it is then turned out of the boxes and laid upon bricks (which absorb the moisture) for two or three days to dry. When sufficiently hard, the pieces are put into the *stove*, a square building fitted up with racks on every side, at proper distances for receiving the pieces, and heated from below. Here they remain in a moderate heat for about two days, till a slimy crust forms on the surface. When taken out of the stove, the crusted part is carefully scraped off, and the remainder, which is now perfect starch, is papered, labelled, and stamped, and placed again in the stove, with a good fire, for about three days, till quite dry. During this drying the lumps crack pretty uniformly into the small pieces in which they appear when sold. The slimes and white waters are treated in the same way, till all the starch is got from them, and boxed, drained, and dried, as before. (See the *Eighth Report of the Commission of Excise Inquiry*, 1834.)

PURE STARCH, from whatever source it is obtained, is a white substance, of a specific gravity about 1.5, insoluble in cold water, but readily soluble* at a temperature between 160° and 180°. Its solution is gelatinous, and by careful evaporation yields a substance resembling gum in appearance, which is a compound of starch and water. Starch is insoluble in alcohol and in ether, and occasions no precipitate in the greater number of metallic solutions; in solution of subacetate of lead, however, it occasions a copious precipitate. The most characteristic property of starch is that of forming a blue compound with iodine; it may be obtained by adding an aqueous solution of iodine to a dilute solution of starch. (See p. 372.) Starch absorbs chlorine, becoming semifluid, brown, and sour, and evolving carbonic and hydrochloric acid.

When a decoction of starch (it should be *pure* and free from gluten) is kept, in or out of the contact of air, for six or eight weeks, water being occasionally added to prevent desiccation, and the temperature between 60° and 80°, a portion of sugar is gradually formed in it. (SAUS-

* I have used the term *solution* of starch, as applicable to the ordinary appearances that ensue, but Raspail has shown that the varieties of starch consist of small brilliant spherules, each of which has a coating less soluble than its interior; that heat bursts these, and lets out their contents, which consist of a gum-like substance, (called by Biot, *dextrine*?) the term *amidine* has also been applied to it. The different varieties of

starch may, it is said, be discriminated by their microscopic characters. Berzelius says, that the action of hot water upon starch is not a true solution, but a swelling up or gelatinization of the starch, and that only a small portion is actually dissolved: but, in reference to the general chemical agencies of starch, it will not be necessary to enter into these distinctions.

SURE, *Ann. de Ch. et Ph.*, xi. 379.) The following table shows more explicitly the nature of these changes*.

	A	B	C	D	E	F
Sugar	37.00	47.4	49.7	35.4	30.4	1.00
Gum	10.00	23.0	9.7	17.5	17.2	0.36
Amidine	14.30	8.9	5.2	18.7	17.0	1.00
Starch	5.83	4.0	3.8	9.4	9.3	98.00
Ligneous starch	10.53	10.3	9.2	7.0	4.4	
Carbonaceous lignin	trace	trace	0.3	trace	0.2	
Soft resin	0.30			loss 6.0		
	77.96	93.6	77.9	94.0	78.5	100.36

A is the composition of the residue of 100 parts of *wheat starch* made into a paste with 1200 of water, and left in a covered but not air-tight saucer for two years; a gray, mouldy, inodorous, semifluid paste, not acid, remained, which, dried at 212° , yielded the above results. B is a similar experiment, in which the starch-paste was kept for thirty-eight days, in a well-corked phial containing a little air. C, the same as B, but air freely admitted. D, a similar paste of *potato starch*, left for forty-two days in a bottle, with a tube cemented into it for carrying off gas: a little hydrogen and carbonic acid were evolved. E, the same as D, but freely exposed. F, the starch-paste as above, left for forty days in a glass vessel filled with carbonic acid. The term *amidine*, in the above table, is applied "to a substance intermediate between gum and starch;" and *ligneous starch* to a product insoluble in boiling water and in many acids, but still becoming purple with iodine. The *carbonaceous lignin* gives a brown colour to the respective solutions. The influence of carbonic acid in preventing the decomposition of starch is strikingly shown by the contents of the last column. If *gluten* be present, starch begins to pass into sugar in a few hours†.

The dilute acids dissolve starch, and the solution, by continued boiling, yields gum and sugar. The conversion of starch into sugar by these means was discovered by Kirchoff, of Petersburg, not accidentally, but in consequence of Napoleon's exclusion of colonial produce from Russia, during the enforcement of what was termed the *Continental System*: his ingenuity was rewarded by the Emperor of Russia, with an annuity of 1000 rubles. His method consisted in boiling with very dilute sulphuric acid. A pound of starch may be digested in 6 or 8 pints of distilled

* The facility with which sugar is sometimes formed is shown in the change which the pulp of many apples undergoes when exposed to air, becoming brown, and at the same time much sweeter. This character belongs to the apples which are preferred for *cyder*, and is obvious by the rapid alteration of colour which they exhibit when cut through so as to expose the interior.

† The change of starch into sugar is always observed during the *germination* of seeds, and in the process of *malting* a similar conversion is effected.

Malt is barley which has been made

to germinate to a certain extent, after which the process is stopped by heat. The barley is steeped in cold water, and is then made into a heap, or *couch*, upon the malt-floor: here it absorbs oxygen, and evolves carbonic acid; its temperature augments, and then it is occasionally turned, to prevent its becoming too warm. In this process the *radicle* lengthens, and the *plume*, called by the maltsters *acrospire*, elongates; and when it has nearly reached the opposite extremity of the seed, its further growth is arrested by drying at a temperature slowly elevated to 150° or more. The

water, rendered slightly acid by 2 or 3 drachms of sulphuric acid. The mixture should be simmered for a few days, fresh portions of water being occasionally added to compensate for the loss by evaporation. After this process, the acid is saturated by a proper proportion of chalk, and the mixture filtered and evaporated to the consistence of syrup; its taste is sweet, and, by purification in the usual way, it affords *granular sugar*. Dr. Tuthill digested a pound and a half of *potato starch* (obtained from about 9 pounds of potatoes) in a mixture of 6 pints of distilled water, and a quarter of an ounce (by weight) of sulphuric acid, at a boiling heat; the mixture was afterwards stirred, and fresh water occasionally added to supply loss by evaporation. After thirty-four hours an ounce of powdered charcoal was added, and the boiling resumed for two hours. The acid was then carefully saturated by lime, and the boiling continued for half an hour, when the liquor was strained through calico. The insoluble residue, after having been washed and dried, consisted of charcoal and sulphate of lime. The filtered liquor was evaporated to the thickness of syrup; and being set aside, became, in eight days, a crystallized mass, resembling brown sugar and treacle. The sugar weighed one pound and a quarter. One pound of it, fermented in the usual way, afforded, on distillation, 14 drachms of proof-spirit. (*Nicholson's Journal*, xxxiii.) MM. de la Rive and Saussure have shown that the contact of air is unnecessary in the above process; that no part of the acid is decomposed, no gas evolved, and that the actual sugar obtained exceeds, by about one-tenth, the original weight of the starch. Hence Saussure concludes that the conversion of starch into sugar depends upon the solidification of water, a conclusion borne out by the comparative analyses. According to Kirchhoff, nitric, hydrochloric and oxalic acids may be substituted in the above process for sulphuric; but phosphoric, tartaric, and acetic acids, are ineffective. The actual nature, however, of the change is not satisfactorily understood, and the experiments showing that starch passes into sugar without the intervention of any acid whatever, render these results doubtful. I shall afterwards have occasion to notice an analogous conversion of wood into gum and sugar.

malt is then cleansed of the rootlets. According to Dr. Thomson, barley loses about 8 per cent. by converting it into malt, of which

- 1.5 is carried off by the steep-water.
- 3.0 dissipated on the floor.
- 3.0 roots separating by cleansing.
- 0.5 waste.

—
8.0

The following are his comparative analyses of unmalted and malted barley, showing the changes which have taken place in the operation.

Gum	5	14
Sugar	4	16
Gluten	3	1
Starch	88	69

—
100 barley 100 malt.

According to Proust (*Ann. de Ch. et Ph.*, v. 337), barley also contains a peculiar substance, insoluble in hot water, which he calls *hordein*, and which, during malting, is diminished in quantity, and converted into sugar or starch. Hitherto *hordein* appears to have been confounded with starch. The following are his comparative analyses:—

	In 100 of Barley.	In 100 of Malt.
Resin	1	1
Gum	4	15
Sugar	5	15
Gluten	3	1
Starch	32	56
Hordein	55	12
	100	100

The *starch* of malt also differs in some of its properties from that of barley.

A true crystallizable compound of starch and sulphuric acid may be obtained by dissolving, in a gentle heat, 1 part of starch in 3 of sulphuric acid, previously diluted with 36 parts of water, and mixing the solution with alcohol, which throws down a precipitate composed of starch and *sulphate of starch*; when washed with alcohol, dissolved in a small portion of water, and left to spontaneous evaporation, acicular crystals of sulphate of starch are formed, from which the free acid, contained in the mother liquor, may be washed with alcohol. These crystals are not perfectly soluble in water without slight decomposition. (SAUSSURE.)

Concentrated sulphuric acid converts starch into a black magma, with the evolution of sulphurous acid: when water is added, more or less carbon is thrown down. Nitric acid easily dissolves starch when warm, and converts it into malic and oxalic acids, without a trace of mucic acid. Hydrochloric acid forms with starch a solution, which, if evaporated, becomes thick and brown. (BERZELIUS.)

With the fixed alkalis starch forms more decided compounds than with the acids. With caustic potassa it produces a combination soluble in water and in alcohol, from which acids separate the starch. Potato starch is more readily dissolved by the alkalis than wheat starch. Lime and baryta form with starch insoluble compounds, which fall when a solution of starch is added to lime or baryta water. When a boiling solution of starch is mixed with subacetate or subnitrate of lead, a white curdy compound falls, and the subsalt becomes neutral. The precipitate consists, according to Berzelius, of 72 starch + 28 oxide of lead. None of the combinations of starch with the salts are interesting or important. It exerts, however, according to Vauquelin, an evident solvent power over phosphate of lime. According to Rose, the presence of starch prevents the precipitation of oxide of iron by the alkalis.

Starch combines with tannin, and the compound is best obtained by filtering a hot solution of starch in infusion of galls; as it cools, the *tannate of starch* falls. It is thrown down when a strong infusion of galls is mixed with one of starch, but the precipitate dissolves on the application of heat. Starch is not thus precipitated by all the varieties of tannin, nor does it apparently combine with artificial tannin.

When starch is heated to 212° , it loses a little in weight from the loss of water, not combined, but adhering, for starch is *anhydrous*. At a somewhat higher temperature it becomes modified in solubility, acquires a slight odour, and is converted into the *amidin* of some chemists. When carefully heated till vapour rises from it, it becomes soluble in cold and hot water, and loses its gelatinous character. Instead of blue, iodine gives it a dingy purple tint. Starch, thus altered by heat, is known in commerce under the name of *British gum*, and is often used as a substitute for gum arabic, in the processes of calico-printing, and for stiffening different goods. It is commonly sold in Paris under the name of *Dextrine*. According to F. Marcet the ultimate components of *torrefied starch* are carbon 35.7, hydrogen 6.2, oxygen 58.1.

The ultimate Analysis of Starch, regarding it as a compound of carbon and the elements of water ($car + q$), has been variously represented in reference to its proximate equivalent, and till this is more accurately

determined, the probable composition of the atom of starch must remain doubtful. If the *amylate of lead* be regarded as a compound of 3 atoms of starch and 1 atom of oxide of lead, the number 96 will be the equivalent of starch, and it will consist of

				Gay Lussac and Thenard.		Prout.	Berzelius.
Carbon .	7	. . 42	. . 43.75	. . 43.55	. . 42.80	. . 44.250	
Hydrogen	6	. . 6	. . 6.25	. . 6.77	. . 6.35	. . 6.674	
Oxygen .	6	. . 48	. . 50.00	. . 49.68	. . 50.85	. . 49.076	
Starch	1	96	100.00	100.00	100.00	100.000	

The following, in other terms, are the comparative results of the ultimate analysis of three varieties of starch, dried at 212°*.

	Wheat Starch.	Arrow-root.	Potato Starch.
Carbon	42.80	44.40	44.25
Water	57.20	55.60	55.75
	100.00	100.00	100.00

* Dr. Prout, referring to the identity in composition between the *sugar* of honey and arrow-root under the ordinary circumstances of the atmosphere, infers that differences exist among the varieties of *amylaceous principles* analogous to those existing among sugars; or, in other words, that there are *low* starches as well as *low* sugars; wheat-starch he places at the head of the starches, and considers arrow-root as the lowest variety. "Whether arrow-root," he observes, "be the lowest that exists, I am unable to say; but I have met with none lower; and have reason to believe that the greater portion of the other varieties of the amylaceous principle known to exist, like the varieties of sugar above given, are intermediate in their composition between arrow-root and wheat-starch."

"The identity of composition between wheat-starch and cane-sugar, and between the sugar of honey and arrow-root, seems to show that, though these bodies are not actually capable of assuming the crystalline form, yet the original tendency among their essential elements to combine in certain proportions (and perhaps to assume certain forms) still continues to operate, though in a mitigated degree, and thus to exert, as it were, a feeble *nisus*, or endeavour toward the maintenance of certain definite modes of existence."

In reference to what are usually called the *extraneous* or foreign ingredients of certain vegetable principles, Dr. Prout has the following remarks:—

"It has been known from the very infancy of chemistry, that all organized bodies, besides the elements of which they are essentially composed, contain

minute quantities of different foreign bodies, such as the earthy and alkaline salts, iron, &c. These have been usually considered as mere mechanical mixtures accidentally present; but I can by no means subscribe to this opinion. Indeed, much attention to this subject for many years past, has satisfied me that they perform the most important functions; in short, that organization cannot take place without them. This point will be more fully investigated hereafter: at present it is sufficient merely to observe, that many of those remarkable changes which crystallized bodies undergo on becoming organized, are more apparent than real; that is to say, their chemical composition frequently remains essentially the same; and the only point of difference that can be traced, is the presence of a little more or less of water, or the intimate mixture of a minute portion of some foreign fixed body. There is no term at present employed which expresses this condition of bodies, and hence, to avoid circumlocution, I have provisionally adopted the term *merorganized*, (*μέρος, pars vel partim*,) meaning to imply by it, that bodies on passing into this state become partly, or to a certain extent, organized. Thus starch I consider as *merorganized* sugar, the two substances having, as we shall see presently, the same essential composition, but the starch differing from the sugar by containing minute portions of other matters, which, we may presume, prevent its constituent particles from arranging themselves in the crystalline form, and thus cause it to assume totally different sensible properties."

INULIN.—This modification of starch was discovered in 1804, by V. Rose, in the root of the *Inula helenium*: it has been found by Payen (*Ann. de Ch. et Ph.*, xxvi. 102), in the tubers of the dahlia, and also in other plants, so that a variety of names have been given to it in reference to its sources, such as *Dahline*, *Menyanthine*, *Datiscin*, &c. Rose obtained it in the form of a white precipitate, deposited during the cooling of a strong decoction of elecampane root. Payen procured it from the grated root of the dahlia, which was first washed with cold water, then boiled with the addition of a little chalk, strained, and filtered through charcoal, and clarified by white of egg: it was then evaporated till a pellicle formed upon the surface; during cooling the inulin was deposited to the amount of 10 per cent. of the original root. The expressed juice of the potato also yields a little inulin (about 3 per cent.) when evaporated.

Inulin is purified by dissolving it in hot water, and cooling the solution, when it is deposited in the form of a white, insipid, inodorous, crystalline powder, specific gravity 1.356. Heated a little above 212°, it loses water and fuses. Iodine renders it yellow. It is insoluble in cold, but sparingly soluble in boiling alcohol: dilute acids dissolve it, and readily convert it, by boiling, into gum and sugar. In other respects, also, it is analogous to common starch.

LICHEN STARCH. LICHENIN.—Most lichens contain a species of starch: it may be obtained from the *Lichen islandicus* as follows: it is cut into shreds, and infused in about 18 parts of cold water, to which carbonate of potassa is added in the proportion of 120 grains to each pound of moss. After 24 hours the moss is drained upon a sieve (not pressed), and thoroughlyedulcorated by cold water: it is then boiled in 9 pints of water down to 6, and the decoction strained and squeezed out whilst hot. The strained liquor, at first clear and colourless, becomes, on cooling, a gray opaque jelly, which, if suspended in a cloth, or dried on blotting-paper, becomes hard as it dries, and of a dark colour. Redissolved in boiling water, it may be again gelatinized. It is tasteless, insoluble in alcohol and ether, contains no nitrogen, and yields on destructive distillation the same products as potato starch. It is only slightly soluble in cold water, and when long and repeatedly boiled, it loses its property of gelatinizing. Iodine renders it dingy green. The dilute acids prevent its gelatinization, and gradually change it into gum and sugar. It is copiously precipitated by subacetate of lead, but, in other respects, resembles common starch.

USES OF STARCH.—Wheat starch is employed for stiffening various fabrics, and articles of wearing apparel*. In applying it to muslin, the addition of borax or of phosphate of soda or ammonia, would at the same time render it so far incombustible, as to prevent burning with flame, and obviate the accidents that so frequently ensue from that cause. A little smalt, prussian blue, or indigo, is generally added to starch to cover its yellowish hue, and to render it more effective in overcoming the tinge that linen and cotton acquire when long worn. In this country, the

* Potato starch is said to be much more hygrometric than wheat starch, and goods which are stiffened with it, are apt to give in damp weather, and to become mouldy if laid by.

consumption of starch, though considerable, is trifling compared with that in Holland and some other parts of the continent of Europe, where stiffly-starched caps and gauzes are much worn by the lower orders: since the abolition of the absurd custom of powdering the hair, there has also been a great falling off in the demand for starch.

Lozenges, and various articles of confectionery, consist partly of starch; and the sugar-plums, sold in the streets, are composed of the refuse parts of the starch mentioned in describing its manufacture, with chalk, gypsum, and other trash: a spurious *refined liquorice* is also made upon the same principle. *Stone-blue* is a compound of indigo or prussian blue and the inferior kinds of starch. Among the substances used to adulterate starch, porcelain-clay was at one time prevalent. Considered as an article of food, as a part of the diet of children and of invalids, and as a component of our most nutritious vegetables, starch is very important, and several of its varieties are often resorted to medicinally. But, although eminently adapted to form part of our food, it is not fitted for exclusive nutriment, and this would appear to be the case with all those proximate principles of vegetables which are deficient in nitrogen.

§ VI. GLUTEN AND ALBUMEN.

MANY plants contain a principle which resembles animal matter, and to which the term *vegeto-animal* matter was formerly applied. Of this substance there are two leading varieties, which may be distinguished by the terms *gluten* and *albumen*.

GLUTEN, so termed from its adhesive character*, is found in many of the esculent seeds, and especially in *wheat*, associated with albumen and starch. Its characteristic properties are, insolubility in cold water, elasticity and adhesiveness when moist, solubility in boiling alcohol, and in some of the acids and alkalis: it is precipitated from some of its solutions by ferrocyanuret of potassium, and by infusion of galls.

When a thick paste of wheaten flour is tied up in a piece of coarse canvass, and washed and kneaded in water till the whole of the starch is extricated and the washings are no longer milky, it leaves a gray, viscid, adhesive, and elastic substance, which consists of gluten and albumen, with a little residue of starch. By boiling this substance in alcohol, it is separable into a soluble and insoluble portion; the soluble part is *gluten*,—the insoluble, *albumen*. *Gluten* is then obtained by mixing the alcoholic solution with water, and distilling off the alcohol: it separates in straw-coloured flocculi, which aggregate, on stirring them together, into an elastic mass, tasteless, and of a peculiar odour: exposed to air, it

* It is the presence of gluten in wheaten flour that renders it pre-eminently nutritious, and its viscosity or tenacity confers upon that species of flour its peculiar excellence for the manufacture of macaroni, vermicelli, and similar pastes, which are made by a kind of wire-drawing, and for which the wheat of the South of Europe, (more abundant in gluten than our own,) is particularly adapted.

The superiority of wheaten over other bread depends upon the great tenacity of its *dough*, which, in *panary fermentation*, is puffed up by the evolved carbonic acid, and retained in its vesicular texture, so as to form a very *light* loaf.

becomes superficially brown and glossy, and gradually dries into a semi-transparent horn-like mass. If obtained by evaporating its alcoholic solution, it is yellow, brittle, and transparent. When moist gluten is digested in acetic acid, the greater part is dissolved, but a peculiar substance, particularly described by Berzelius (*Lehrbuch*), remains. When the acetic solution of gluten is evaporated, it leaves a colourless transparent residue; saturated by caustic or carbonated ammonia, a flocculent precipitate falls, having all the characters of the original gluten. When a solution of gluten in acetic acid, or in alkali, is mixed with sulphuric, nitric, or hydrochloric acid, the gluten separates apparently with its original characters, but, in fact, chemically combined with the precipitant acid. Neither acetic nor phosphoric acid precipitates gluten from its alkaline solution, and yet phosphoric acid has no especial solvent power on moist gluten. When the solution of gluten in caustic potassa is evaporated at a low temperature (below 110°), a white, opaque, and apparently neutral compound of gluten and potassa remains. Caustic ammonia has little solvent power over gluten in its ordinary viscid state, but an acid solution of gluten is not permanently precipitated by ammonia. The combinations of gluten with other bases are insoluble in water, and are precipitated when the solution of gluten in potassa is mixed with the earthy or metallic salts. The carbonated alkalis scarcely dissolve gluten, and when it is precipitated by them from its acid solutions, they do not redissolve the precipitate. The alkaline and acid solutions of gluten give a white precipitate with corrosive sublimate; and when viscid gluten is put into a solution of corrosive sublimate, it shrinks, hardens, and loses all tendency to putrefy. An acetic solution of gluten is not affected by acetate or subacetate of lead, or by sulphate of iron, but is abundantly precipitated by infusion of galls.

ALBUMEN is the portion of the original glutinous residue of wheat flour, which is insoluble in alcohol; it remains in the form of a gray substance after the extraction of the gluten; it is easily dried, and becomes brittle and pulverulent. Taddei called this insoluble part of the viscid gluten of wheat *Zinoma* (from ζυμη, leaven or ferment), and the soluble portion, which we have above described as *gluten*, he called *Gliadine* (from γλια, glue). When this form of vegetable albumen is subjected to the action of weak caustic potassa, it swells, softens, and dissolves: this solution, like that of animal albumen, gives precipitates with most of the earthy and metallic salts, and is not permanently precipitated by phosphoric or acetic acids, but the stronger acids coagulate it. When vegetable albumen has been dried, it is no longer soluble in acetic and phosphoric acids, but swells up and becomes transparent, and if then boiled in water, it increases in bulk and loses its yellow tint, but is not dissolved. Veg-albumen is insoluble in carbonated alkalis; it is precipitated from its solutions by carbonate of ammonia, by ferrocyanuret of potassium, and by tincture of galls. Corrosive sublimate throws it down, where there is no excess of acid present.

Kirchoff and Saussure have made us acquainted with the remarkable action which gluten exerts upon starch. Two parts of starch are mixed with 4 of cold water, and gradually added to 20 parts of boiling water;

a thick paste is formed, to which 1 part of finely-powdered gluten is added, and the mixture kept six or eight hours in a temperature between 120° and 170° ; under these circumstances it becomes thin, clear, and sweet; part of the starch is converted into gum and sugar, a little carbonic acid is evolved, but no oxygen absorbed, and on evaporating to dryness, the residue amounts to the joint weight of the starch and gluten employed.

Kirchoff has shown that a small quantity of gluten is capable of thus saccharizing a large quantity of starch, and has pointed out the application of this fact to the production of sugar in *worts* and *wash*, and the consequent formation of alcohol when such liquors are fermented.

Gluten is a constituent of barley and rye; and a modification of it, under the name of *legumine*, is found in pease and beans. (See EINHOF, BERZELIUS, and BRACONNOT, *Ann. de Ch. et Ph.*, xxxiv. 68.) The gluten of barley is an important agent in the change which that grain suffers in conversion into *malt*, and the action of ground malt upon viscid starch is analogous to that of gluten. Payen terms the saccharizing principle of malt or barley *diastase*, and regards it as the agent by which starch is converted into sugar during the germination of seeds and the expansion of buds.

All seeds which form an emulsion with water, contain a principle analogous to, if not identical with, albumen: it has sometimes been termed *emulsin*. In almond-emulsion this substance is mixed with oil; it may be separated by boiling, by which it is coagulated, and the adherent oil may be abstracted either by ether, or by absolute alcohol: the residue is *emulsin*. (*Albumino-caseum* of Payen and O. Henry.) The curious mutual action of emulsin (or *synaptase*) and amygdalin is noticed in a subsequent section. (See *Amygdalin*.)

The *milk of the cow tree*, which flourishes in the mountainous regions of Quito in America, and, according to Boussingault and Mariano de Rivero, closely resembles cow's milk in taste and appearance, and the milk of the *Carica Papaya*, examined by Vauquelin, contain peculiar modifications of gluten; and the same substances may be extracted from other *milky juices* of plants, instances of which will afterwards be adduced.

Yeast, which separates from *must* and *wort* during fermentation, has many of the properties of gluten.

All the substances which have been mentioned in this section are so far analogous, that their aqueous solutions undergo, under favourable circumstances, changes resembling those of putrefying animal matter. The plants which bear *cruciform flowers*, also contain a similar principle, and hence the offensive stench that arises from them whilst rotting in heaps, and their efficacy as *manures*; it is apparently the presence of *nitrogen*, as one of the ultimate elements of these plants, that gives them their peculiarities, and tends to the production of ammonia during their decomposition; but the whole of this subject has been as yet only imperfectly investigated. *Gluten* has been subjected to ultimate analysis with the following results.

	F. Marcet.	Zenneck.
Carbon	55.7	45.80
Hydrogen	7.3	3.37
Oxygen	22.0	30.33
Nitrogen	14.5	20.50
	100.0	100.00

POLLENIN.—The pollen of flowers contains a peculiar vegeto-animal principle, which was first distinguished by Fourcroy and Vauquelin in their examination of the pollen of the *date tree*, and afterwards by John in his analysis of the seeds of the *lycopodium*, and of the pollen of the *tulip*. It is insoluble in water, alcohol, ether, oils, and alkalis, and highly inflammable, so that when thrown into a flame it burns with a kind of deflagration; hence lycopodium is used to produce theatrical lightning, being much cleaner and more brilliant and rapid in its combustion than resin. When pollen is digested in caustic potassa it exhales ammonia, and when subjected to destructive distillation ammonia is one of the products.

§ VII. LIGNIN.

THIS term is aptly applied to *woody fibre*, as it exists in the ligneous parts of trees and plants; but as with other proximate principles, there are several modifications of it, and although in its ordinary state it appears to be indigestible, it is easily modified by heat and other agents so as to be converted into gum and sugar; and in a highly-attenuated state of organization it forms an esculent, and probably nutritive part of many fruits and vegetables. As constituting the bulk of different woods, and as forming vegetable fibre, its applications in the arts of life are highly interesting and useful; its chemical properties therefore acquire a proportionate degree of importance.

The term *lignin* is generally applied to the fibrous residue which remains after the different principles already enumerated, and others, afterwards to be described, are extracted by various solvents; hence *insolubility* in water, in alcohol, and in dilute acids and alkalis, is one of its more obvious characters. It is also recognised as the most durable product of vegetation, and the extreme perfection in which it is occasionally found in mummy-cases, in ancient buildings, as in the piles of bridges, and even in submerged forests, shows its power of resisting decay. When, however, it is long exposed to the joint energies of air and moisture, it often becomes pulverulent, acquiring a brown or gray colour, as we see in the rotten wood of very old trees. It is also liable to more rapid decay and disintegration under the influence, probably, of parasitic plants, especially where the place is damp, and air imperfectly admitted, as in cases of what is termed *Dry-rot*. In some cases it is entirely decomposed, leaving only a carbonaceous residue.

The density, and other mechanical properties of wood, are very various; its texture is porous and vascular, and what is usually termed *fibrous*, so that it splits more easily in one direction than in another. In its ordinary state, exclusive of lignin, it contains various soluble and other matters, which confer upon it various characters as to colour, smell, taste, and uses, and the proportion of these varies in the same tree at different seasons, and at various periods of its growth. The recent wood of trees loses by drying, and by the action of ordinary solvents, from 1 to 10 per cent. About 95 per cent. of *lignin* is the average produce of the common woods. The apparent low specific gravity of wood is referable to its porosity, the density of lignin, or of wood free from air, varying, appa-

rently, from 1.4 to 1.58. There are a few of the heaviest woods, such as box, guaiacum, and ebony, which are, in their ordinary states, denser than water.

Chlorine gradually bleaches lignin, and the varieties of wood and woody fibre may in this way be rendered perfectly white, as in the process for bleaching linen and cotton, in which, by the alternate action of weak acids and alkalis, and exposure to light, air, and moisture, or by the occasional employment of chlorine or its compounds, the colouring matters are gradually abstracted or decomposed. Concentrated sulphuric acid gradually converts wood into a modification of gum, care being taken to keep it cold; and when diluted and boiled, sugar is formed, as observed in regard to starch, so that linen rags may be thus converted into sugar*. When sawdust and sulphuric acid are heated together, a black magma is produced, which, on dilution with water, deposits between 40 and 50 per cent. of carbonaceous residue. Nitric acid tinges wood yellow, and gradually disintegrates and decomposes it, producing oxalic acid. Paper, which is merely another form of lignin, is gelatinized by cold sulphuric acid: cold nitric acid converts it also into a gelatinous pulp, which is sometimes partially blued by iodine, and therefore appears to contain starch. Hydrochloric acid renders wood brown and black, but does not dissolve or further decompose it. The weak alkaline solutions exert scarcely any action on wood; but when heated with caustic potassa it is changed into a brown soluble matter, which appears to contain a peculiar extractive matter, like ulmin, and acetic acid. Wood combines with some of the salts, and others it decomposes. It combines with alumina, when steeped in solutions of alum or acetate of alumina; and when digested in solution of corrosive sublimate, a compound results, which resists decay, under circumstances tending to rot unprepared wood. Sulphate of copper, sulphate of iron, and several other salts, are capable of forming analogous combinations. It is upon these attractions of woody fibre that the art of dyeing and of calico-printing mainly depend, for linen and cotton are, as I have already observed, mere modifications of lignin: paper also is made of linen or cotton rags; and hay, straw, leaves, and shavings of wood may, by proper means, be reduced to a pulp capable of being formed into paper.

The action of heat upon wood, under different circumstances, is extremely interesting, as the following outline of this part of its history shows. When wood is thoroughly dried at a temperature of about 220° it shrinks and splits, or if in powder loses variably in weight, depending upon its humidity: it again absorbs moisture from the air. When wood

* We are indebted to M. Braconnot for some highly-interesting experiments, relating to the action of sulphuric acid on wood. (*Ann. de Ch. et Ph.*, xii. 172.) In the course of these researches, he triturated 25 parts of hempen cloth with 34 of the acid: it acquired the consistency of mucilage, which, after 24 hours, was almost entirely soluble in water. The diluted liquor was saturated with chalk, filtered, and evaporated to the consistency of syrup; it deposited sul-

phate of lime, and was then further evaporated to dryness, when a substance, having the characters of gum, was obtained. In another experiment, 24 parts of lignin were reduced to gum by 34 of sulphuric acid; this acid mixture, diluted with water, and boiled for 10 hours, became sweet; the acid was then separated by chalk, and the liquor, on due evaporation, afforded a crystallizable sugar.

is carefully baked, so as to become of a pale-brown colour, it acquires solubility in water to some extent, yielding a brown infusion, which, when carefully prepared, tastes and smells like *toast and water*: and, indeed, under proper management, it may be converted into a palatable and nutritious bread. Something of this kind is used by the peasantry of Norway and Sweden; and the following directions are given for the purpose by Professor Autenrieth of Tübingen; he employed *beech* and similar woods, destitute of turpentine. "In the first place, everything that was soluble in water was removed by frequent maceration and boiling. The wood was then reduced to a minute state of division, that is to say, not merely into fine fibres, but actual powder; and after being repeatedly subjected to the heat of an oven, was ground in the usual manner of corn. Wood thus prepared, according to the author, acquires the smell and taste of corn flour. It is, however, never quite white, but always of a yellowish colour. It also agrees with corn flour in this respect, that it does not ferment without the addition of leaven, and in this case sour leaven of corn flour is found to answer best. With this it makes a perfectly uniform and spongy bread; and when it is thoroughly baked, and has much crust, it has a much better taste of bread than what in time of scarcity is prepared from the bran and husks of corn. Wood flour also, boiled in water, forms a thick, tough, trembling jelly, like that of wheat starch, and which is very nutritious." (PROUT, *Phil. Trans.*, 1827.)

When wood is burned in the air, it affords large quantities of inflammable gases which produce flame and render it a valuable fuel; and if decomposed with a partial access of air only, it leaves common charcoal, the relative proportions of which, as afforded by the different kinds of wood, have already been noticed. Subjected to destructive distillation in close vessels, *water*, *empyreumatic oil* and *tar*, *pyroxylic spirit*, and *acetic acid*, together with gaseous compounds of carbon and oxygen, and carbon and hydrogen, are the results. These, and the various products into which they are resolvable, have lately attracted the attention of several chemists, and will require more detailed notice.

ULTIMATE COMPOSITION OF LIGNIN.—With regard to the ultimate elements of lignin, Gay Lussac and Thenard first rendered it probable that the hydrogen and oxygen in this principle exist in it in the proportions in which they form water. The variety of forms in which lignin occurs in different woods is so great as to render a separate examination of each of them impossible; Dr. Prout, therefore, selected *two* for the purpose of analysis, viz., the woods of the *Box* and *Willow*, which appeared to present the greatest contrast; the one being amongst the densest, the other the lightest of the woods. These were both treated exactly in the same manner; that is to say, they were first reduced to the form of a coarse powder by rasping, then well pulverized in a Wedgwood mortar, and afterwards sifted. Being by these means reduced to the form of impalpable powders, they were boiled in repeated portions of distilled water, till that fluid came off unchanged. After this they were similarly treated with alcohol, and finally again with distilled water. They were now exposed to the atmosphere, when in a dry and favourable state; and

when they ceased to lose weight were submitted to analysis, and found to yield (abstracting foreign matters)

	Box.	Willow.
Carbon	42.7	42.6
Water	57.3	57.4
	100.0	100.0

A known weight of each was then exposed for twenty-four hours to a temperature of 212°, and afterwards for six hours longer (by means of an oil-bath) to a temperature between 300° and 350°; and at the end of this time the box had lost 14.6 and the willow 14.4 per cent. Analyzed in this state of desiccation, they were found to consist of

	Box.	Willow.
Carbon	50.0	49.8
Water	50.0	50.2
	100.0	100.0

showing that the loss of weight arose from the escape of water. These latter results nearly agree with those of Gay Lussac and Thenard, as obtained from the analyses of the woods of the *Oak* and *Beech*, and seem to show, beyond a doubt, that the composition of all of them is similar, or that they consist of *equal weights of carbon and water*; to which simple analogy, Dr. Prout observes, this important principle probably owes its stability.

We have no satisfactory data from which the proximate atomic weight of lignin can be inferred, so that assuming it at its lowest equivalent, it may be regarded as composed of

				Prout.	Gay Lussac and Thenard.
Carbon	3	18	50.00	49.80	51.45
Hydrogen	2	2	5.56	5.58	5.82
Oxygen	2	16	44.44	44.62	42.73
Lignin	1	36	100.00	100.00	100.00

The *Proximate Vegetable Principles* now examined constitute the principal *nutritive* ingredients in vegetable food, and with the exception of gluten and albumen, appear to be, in reference to ultimate composition, *hydrates of carbon*.

The following table, drawn up by Sir H. Davy, exhibits the relative proportions of soluble matter contained in 1000 parts of the different vegetable substances enumerated in the first column (*Agricultural Chemistry*, 4to., p. 131):—The deficiency may be considered as water, and inert insoluble substances; and the soluble matters may be regarded as those upon which the nutritive powers of the different vegetables depend. The relative quantity of nitrogen contained in several of the articles of this table has been ascertained by Boussingault. (*Ann. de Ch. et Ph.*, lxvii. 408.)

VEGETABLE SUBSTANCES.	Whole quantity of Soluble or Nutritive Matter.	Mucilage or Starch.	Saccharine Matter or Sugar.	Gluten or Albumen.	Extract, or matter rendered insoluble during evaporation.
Middlesex wheat, aver. crop	955	765	—	190	—
Spring wheat	940	700	—	240	—
Mildewed wheat of 1806	203	171	—	32	—
Blighted wheat of 1804	650	520	—	130	—
Thick-skinned Sicilian wheat of 1810	955	725	—	230	—
Thin-skinned Sicilian wheat of 1810	931	722	—	239	—
Wheat from Poland	950	750	—	200	—
North American wheat	955	730	—	225	—
Norfolk barley	920	790	70	69	—
Oats from Scotland	743	641	15	87	—
Rye from Yorkshire	792	645	38	109	—
Common beans	570	426	—	103	41
Dry pease	574	501	22	35	16
Potatoes	from 260 to 200	from 200 to 155	from 20 to 15	from 40 to 30	—
Linseed cake	151	123	11	17	—
Red beet	149	14	121	14	—
White beet	136	13	119	4	—
Parsnep	99	9	90	—	—
Carrots	98	3	95	—	—
Common turnips	42	7	34	1	—
Swedish turnips	64	9	51	.2	2
Cabbage	73	41	24	8	—
Broad-leaved clover	39	31	3	2	3
Long-rooted clover	39	30	4	3	2
White clover	38	29	1	3	5
Sainfoin	39	28	2	3	6
Lucerne	23	18	1	—	4
Meadow fox-tail grass	33	24	3	—	6
Perennial rye grass	35	26	4	—	5
Fertile meadow grass	78	65	6	—	7
Roughish meadow grass	40	29	5	—	6
Crested dog's-tail grass	35	28	3	—	4
Spiked Fescue grass	19	15	2	—	2
Sweet-scented soft grass	82	72	4	—	6
Sweet-scented vernal grass	50	43	4	—	3
Fiorin	54	46	5	1	2
Fiorin cut in winter	76	64	8	1	3

§ VIII. VEGETABLE EXTRACT. ULMIN.

UNDER the term *extract*, the pharmaceutical chemists originally included all substances capable of being extracted from vegetable products by decoction in water, and of being obtained in a solid form by evaporation. It might of course contain all the preceding substances included in this chapter, and others afterwards to be mentioned; its properties were therefore extremely various and indefinite. They afterwards endeavoured to distinguish its varieties by the terms bitter, sweet, mucilaginous, astringent, narcotic, colouring, and resinous extracts, &c.; but

in general, any brown residue obtained by boiling down the decoctions, or infusions, or even the expressed juices of vegetables, was distinguished by the generic term *extract*. Boerhaave first pointed out the existence of a peculiar substance in these extracts, soluble both in alcohol and in water, which he called *Materia hermaphrodita*. Scheele called it *Materia saponacea*; and Vauquelin afterwards gave the name *extractive matter* to what he regarded as a peculiar vegetable principle, soluble in water and alcohol, insoluble in ether, and becoming insoluble in water by long-continued boiling, and by exposure to light and air.

It seems probable that the *brown extractive*, obtained by the above processes, is not pre-existent in the vegetables whence it is obtained, but principally a *product* of the action of heat, water, air, and other agents; the different colouring-matters of plants have also been termed *coloured extractive*, but these we shall consider separately*. It will also be found in regard to many of the pharmaceutical extracts, that their activity resides in some peculiar and distinct proximate product, mixed with other unimportant and inactive substances, and these must also be distinctly considered.

ULMIN.—The term *extractive* is perhaps most appropriately applied, in a strict chemical sense, to the peculiar brown matter which may be extracted from bog-earth, peat, and turf; it is frequently termed *humus*, or *humine*, (*Moder* of the Germans, *Gëine* of Berzelius.) There is also a brown exudation found upon the barks of trees, and especially of the elm, and hence called *ulmin*, which contains a similar matter combined with potassa. Lastly, the action of heat, acids, alkalis, and some other chemical agents, upon a variety of organic products, is attended by the production of more or less of a similar matter. As it combines with bases, Boullay terms it *ulmic acid*; and according to him, the brown matter occasionally produced by the decomposition of hydrocyanic acid, contains it united with nitrogen; this he calls *azulmic acid*. (*Ann. de Ch. et Ph.*, xliii. 273.) He represents ulmin, or ulmic acid, as a compound of 56·7 per cent. carbon, and 43·3 hydrogen and oxygen in the proportions to form water: he considers it as the most important ingredient in the soil as relates to its nutritive powers. Malaguti is quoted by Dumas (*Chim. app. aux Arts*, v. 399), as having obtained *crystallized ulmic acid* by the long-continued action of very dilute nitric acid upon sugar at a boiling heat.

*Ulm*in, or *ulmic acid*, may be obtained by digesting the brown exudation of the elm in boiling water, and precipitation by an acid. Rotten leaves, bog-earth, wood-soot, or turf, may be digested in a weak solution of caustic or carbonated potassa, by which a brown liquid is obtained (*ulmate of potassa*), from which acids throw down ulmin. Braconnot

* In preparing *extracts* for pharmaceutical use, the greatest care must be taken to avoid injuring them by heat, and they should accordingly be evaporated in a water-bath, or by steam not exceeding 212°. It is easy to evaporate at lower temperatures, as in vacuo, or even over sulphuric acid, and many of the extracts used in medicine may be so

obtained, of much greater activity than when prepared in the usual way: but for medical use this is perhaps not desirable; *uniformity* is the great object, and whether half a grain or two grains of the more powerful extracts is a dose, is of less importance than the certainty that they are as far as possible of a given power.

procures it (*Ann. de Ch. et Ph.*, xii. 192) by heating equal weights of caustic potassa and sawdust, or shavings of wood, with a little water, in a silver crucible, continually stirring the mixture: when it suddenly boils up, it is removed from the fire, and stirred till cold, so as to expose it as much as possible to the air, for the formation of ulmic acid in this case depends upon the absorption of oxygen. When cold, the product is dissolved in water, filtered, and decomposed by diluted sulphuric acid; the precipitated ulmic acid is then washed and dried.

Ulmic acid varies in appearance according to its state and source: when recently precipitated it is in brown flocks; but when dried, brittle and resin-like. It is nearly tasteless, almost insoluble in water, but communicates a brown tinge to it. Sulphuric acid dissolves it, but lets it fall on dilution, and it then retains a little acid: it combines and forms soluble compounds with the alkalis; with the alkaline earths, and many of the other oxides, it produces combinations which are insoluble or difficultly soluble; but the characters of these compounds, as given by different authorities, are much at variance. Some of the metallic salts precipitate it so completely as to leave the supernatant liquid colourless. Some of its compounds form useful pigments (*Umbers* are of this description?) and may be employed in dyeing and calico-printing.

BITTER EXTRACTIVE.—Whether any peculiar organic product does or does not give rise to the bitter flavour of many of the pharmaceutical extracts, such as those of *quassia*, *wormwood*, *centaury*, and others, from which no distinct crystallizable substance has hitherto been obtained, or whether it is a property belonging to *extractive*, without conferring upon it any distinctive character beyond that of bitterness, are questions which still remain to be decided. The existence of the intensely bitter and definite compounds called *vegeto-alkalis*, leads to the suspicion of some analogous source of bitterness in other cases, but there are many plants in which these cannot be detected, and in which the bitterness seems to reside in a principle having the essential characters of *extractive*. The following are some of the most important of them.

Aloe-bitter. The substance known in commerce under the name of *aloes*, is the extract of several species of aloe, such as the *spicata*, *vulgaris*, &c. It is brown, sometimes translucent and sometimes opaque, and of a peculiar odour, especially when breathed upon: it is almost entirely soluble in water and in common alcohol; the portion insoluble in water has not the characters of a resin, but appears to be oxygenized extractive. When its aqueous solution is cautiously evaporated it leaves a brown residue, soluble in water, but insoluble in ether and in anhydrous alcohol. Chlorine throws down from its aqueous solution a brown substance, resembling the original insoluble part. Sulphuric acid dissolves it without apparent change; cold nitric acid dissolves it and acquires a greenish tint, and when the solution is heated malic and oxalic acids are formed, and a red resinous substance, of an agreeable odour. When 1 part of aloes is dissolved in 8 of nitric acid, and evaporated to dryness, the residue is yellow and intensely bitter; it deflagrates when heated, and communicates a deep purple tint to water, and to alkaline solutions. It forms yellow solutions in the acids, and is not precipitated by the salts

which throw down unaltered extractive. (BRACONNOT, *Ann. de Ch. et Ph.*, LXVIII. 24.)

From *rhubarb-root*, *squills*, *briony*, *gentian*, and several other drugs, bitter substances have been extracted, but none of them are possessed of sufficiently distinctive characters to enable us to consider them as *proximate bitter principles*: such as are most definite, or crystallizable, will be noticed in another section.

Artificial Bitter.—By digesting indigo, silk, and a few other substances, both of vegetable and animal origin, in nitric acid, an intensely-bitter matter is formed, called by Welther the *yellow bitter principle*. (*Ann de Ch.*, XXIX.) Chevreul has rendered it probable that this is a compound of a peculiar product with nitric acid. It is crystallizable, burns like gunpowder, and detonates when struck with a hammer.

§ IX. ASTRINGENT EXTRACTIVE. TANNIN. TANNIC ACID.
GALLIC ACID. ELLAGIC ACID. PYROGALLIC ACID. METAGALLIC ACID.

THERE are numerous vegetables which have more or less of an *astringent* flavour, and of which the aqueous decoctions or infusions occasion a precipitate in solutions of animal jelly, and in those of several metallic salts: they change the persalts of iron to dark blue or dingy green. These well-marked properties have been long ascribed to a peculiar proximate principle, designated *tannin*, as being essential to the conversion of skin into leather: its power of combining with salifiable bases led some chemists to term it an *acid*, and it appeared in many cases to be associated with, and sometimes apparently a modification of *gallic acid*. It has, however, been obtained in a distinct form by Pelouze (*Ann. de Ch. et Ph.*, LIV. 337), and its characters are such that it may be appropriately termed *tannic acid*. But the properties of the vegetable infusions and decoctions containing *astringent matter*, are not solely referable to tannic acid, but appear to depend upon its association with extractive, and in some cases with gallic acid; hence the varied effects which they produce when tested by the above-mentioned reagents, and the division (adopted by some chemical authors) of astringents into two classes, namely, those producing *blue* or *black*, and those producing *green* precipitates with persulphate of iron.

The relative proportion of tannin, in different vegetables, may be tolerably-well judged of by the weight of the precipitate which they afford in a strong solution of isinglass. The following table, by Cadet, shows the relative weights of the precipitates formed by an infusion of 100 parts of the respective substances.

Galls	36	Weeping-willow bark	16
Tormentil root	50	Bohemia olive bark	16
Alder bark	36	Bark of <i>Coryaria myrtifolia</i>	13
Apricot bark	32	Bark of <i>Rhus typhinum</i>	10
Pomegranate rind	32	Green acorn cups	10
Oak bark	25	Service-tree bark	8
Cherry-tree bark	24	Horse-chestnut bark	6
Bark of the <i>Cornus mascula</i>	19	American sumach bark	6
Plane-tree bark	16		

In the following table, the first column shows the whole quantity of extract obtained from 100 parts of the different substances, and the second column the proportion of tannin in that extract. (DAVY.)

	Extract.	Tan con- tained in it.		Extract.	Tan con- tained in it.
Galls	37.5	26.4	Entire willow bark	2.2	2.2
Inner bark of oak	23.5	16.0	Sumach	34.3	16.2
— horse-chestnut	18.5	15.2	Souchong tea	32.5	10.0
Entire oak bark	12.7	6.3	Green tea	8.5	8.5
— horse chestnut do.	11.0	4.3	Catechu from Bombay	54.3	54.3
— elm bark	2.7	2.7	— Bengal	48.1	48.1

The average quantity of tannin in 480 lbs. of different barks, is as follows. (DAVY, *Agricul. Chem.*)

	lb.		lb.
Entire bark of middle-sized oak, cut in spring	29	Entire bark of Lombardy poplar	15
— Spanish chestnut	21	— Birch	8
— Leicester willow, large size	33	— Hazel	14
— Elm	13	— Black-thorn	16
— Common willow, large	11	— Coppice oak	32
— Ash	16	— Oak, cut in autumn	21
— Beech	10	— Larch, cut in autumn	8
— Horse-chestnut	9	White interior cortical layers of oak bark	72
— Sycamore	11		

The infusions and decoctions of vegetables containing tannin, not only affect solutions of jelly and of peroxide of iron, as above stated, but they also precipitate the salts of lead, tin, copper, and indeed of most of the metals: these precipitates are of variable composition, and often contain extractive, and tannin and gallic acid.

The following plants contain the modification of tannin which renders solutions of peroxide of iron deep-blue. (GMELIN.) *Galls*; the roots of *Lithrum salicaria*, *Geum urbanum* and *rivale*, *Potentilla argentea* and *anserina*, *Sanguisorba officinalis*, *Poterium sanguisorba*, *Alchemilla vulgaris*, *Arctium lappa*, *Polygonum bistorta*, *Iris pseudacorus*, *Nymphaea alba*; the wood of the oak, and many other trees; the bark of different species of oak; the twigs of the black currant and of sumach; the leaves of oak, *Uva ursi*, and many others; the petals of pomegranate, *Rosa gallica*, and *Paeonia officinalis*.

The tannin which gives a green precipitate with persalts of iron, is found in catechu and in kino; in the roots of the *Tormentilla erecta*, *Potentilla reptans*, *Rosa canina*, *Rhæum rhaponticum*, &c.; in the different species of Cinchona bark, in cinnamon, cassia, and in horse-chestnut bark; in the leaves of *Salvia officinalis*, *Lanium album*, *Glecoma hederacea*, &c.; in the varieties of tea; in the flowers of *Tilia Europæa*, *Centaurea cyanus*, and *Arnica montana*; in horse-chestnuts, date-stones, &c.

Several processes have been suggested for the separation of pure tannin from the solutions in which it is combined with other vegetable principles; they generally consist in throwing it down in combination either with sulphuric acid, which is afterwards abstracted by carbonate of lead or carbonate of baryta; or by subacetate of lead, or chloride of tin,

the tannates of lead or tin, which fall, being afterwards decomposed by sulphuretted hydrogen. In these cases, solutions of a more or less pure tannin are obtained, which are filtered through animal charcoal, and cautiously evaporated. But tannin, as we shall presently find, is very prone to change, and the action of acids, bases, salts, and sulphuretted hydrogen, probably tend to modify it; hence the preference due to the following process, suggested by Pelouze, and which appears unexceptionable. The lower opening of an elongated glass vessel is loosely closed by a piece of linen, or a plug of tow, and it is then half filled with powdered galls gently pressed down: *common* ether (hydrous ether) is then poured in, and the upper orifice being closed so as to admit a little air, but prevent evaporation, it slowly filters through the galls into the vessel underneath, where it forms two distinct liquids; the one light and very fluid, the other more dense and slightly yellow; more ether is poured in above till the lower stratum of liquid no longer is increased in quantity. The liquids are then poured into a funnel, the tube of which is at first stopped by the finger, and, when they have separated into two portions, the heaviest is drawn off into a capsule, and the lighter put aside for distillation, it being chiefly ether. The denser liquid is then purified by washing it with anhydrous ether, from which it is separated as before, and ultimately evaporated in a stove, or under the receiver of the air-pump; a spongy product is obtained, not crystalline, white, or with a slight yellow tint, and amounting to from 35 to 40 per cent. of the galls employed. It is tannin, as pure as it can be procured*.

TANNIC ACID, or TANNIN, in this state, is eminently astringent, without any bitterness, inodorous, and, though very sparingly soluble in water, the solution reddens litmus. It decomposes the alkaline carbonates with effervescence, and forms insoluble precipitates in the greater number of metallic solutions, which are true *tannates*. The pure protosalts of iron are not altered by it, but in the persalts it occasions an abundant dark-blue precipitate. It is less soluble in anhydrous alcohol and ether than

* *Artificial Tannin*.—Mr. Hatchett has shown that a species of tannin may be formed artificially by digesting charcoal in dilute nitric acid during several days; it is at length dissolved, and a reddish-brown liquor is obtained, which furnishes, by careful evaporation, a brown glossy substance, amounting to about 120 parts from 100 of charcoal.

This *artificial tannin* differs in one circumstance from natural tannin, which is, that it resists the action of nitric acid, by which all the varieties of natural tannin are decomposed, though some are more capable of resisting its action than others.

Artificial tannin has a bitterish astringent taste, is soluble in water and alcohol, and forms an insoluble precipitate in solutions of animal gelatine, the precipitate consisting, according to Mr. Hatchett, of

36 tannin
64 gelatine

100

Hydrochloric and sulphuric acids occasion brown precipitates, in solution of artificial tan, which are soluble in hot water. It combines with the alkalis, and forms a precipitate of difficult solubility in aqueous solutions of lime, baryta, and strontia, and most metallic solutions: these precipitates are of a brown colour.

A variety of artificial tan is formed by digesting camphor and resins in sulphuric acid, till the liquor becomes black, and on being poured into water, deposits a black powder, which, by digestion in alcohol, furnishes a brown matter, soluble in water, and forming an insoluble precipitate with gelatin. (HATCHETT, *Phil. Trans.*, 1805, 1806.)

in water. It cannot be crystallized. It burns upon platinum-foil without residue. Its concentrated solution is precipitated *white* by hydrochloric, nitric, sulphuric, phosphoric, and arsenic acids: it is not affected by tartaric, oxalic, lactic, citric, acetic, succinic, selenious, or sulphurous acids. Heated with nitric acid it is rapidly decomposed, and oxalic acid is formed. With cinchonia, quinia, morphia, codeia, brucia, and strychnia, it forms white precipitates, sparingly soluble in water, but very soluble in acetic acid.

The aqueous solution of tannic acid may be long preserved without change, provided air be excluded, but in open vessels it absorbs oxygen, evolves carbonic acid, becomes turbid, and deposits *gallic acid*, into which, therefore, it is converted; this is the reason why recently-prepared infusion of galls precipitates several substances (in the form of tannates) which it will not throw down after long exposure to air, its tannin having then passed into gallic acid. This is especially the case with solutions of morphia, the tannate of which is insoluble, but the gallate, soluble.

Tannin forms a white precipitate in solution of gelatin (*tannogelatin*), which, when carefully dried, becomes hard and tough; if gelatin predominate, the precipitate may be redissolved by heat in the supernatant liquid; but if the tannin be in excess, the precipitate becomes elastic and agglutinated. Tannogelatin dried at 212° consists of about 54 tan, and 46 gelatin. Tannin cannot, in this way, be wholly separated from its solutions by a solution of gelatin, but when a piece of skin, previously cleansed and soaked in lime-water (as it is prepared for tanning) is used, it absorbs the whole of the tannic acid, leaving in solution any gallic acid that might have been present. Tannin precipitates albumen and vegetable gluten.

When gelatinous alumina is agitated with solution of tannin, it rapidly absorbs it, forming an insoluble precipitate, and the filtered liquor does not discolour persulphate of iron: this is not the case with gallic acid.

When tannin is subjected to the temperature of boiling oil, water, carbonic acid, and metagallic acid are formed. Dried at 240° it is not decomposed, but becomes anhydrous. In this state it consists of*

	Berzelius.				Pelouze.
					<i>mean of 4 expts.</i>
Carbon . . .	13	108	50.70	52.69	51.56
Hydrogen . . .	9	9	4.23	3.86	4.20
Oxygen . . .	12	96	45.07	43.45	44.24
	<u>1</u>	<u>213</u>	<u>100.00</u>	<u>100.00</u>	<u>100.00</u>

but its equivalent deduced from the neutral tannates, is $213 \times 2 = 426$, so that our symbol *tan'* represents $(36 \text{ car} + 18 \text{ h} + 24 \text{ o}) = 426$.

TANNATE OF POTASSA.—When solution of tannic acid is added to a solution of caustic potassa or its carbonate, a precipitate falls, scarcely soluble in alcohol or water; it forms a gelatinous compound when hydrated, and when dry, assumes an earthy aspect.

TANNATE OF SODA is more soluble than tannate of potassa.

* The tannin of catechu is said to contain less oxygen than that of galls: *tannous acid*?

TANNATES OF BARYTA, STRONTIA, and LIME, are difficultly soluble in water, but they dissolve in excess of tannic acid, and in acetic acid.

TANNATE OF PEROXIDE OF IRON. ($fe + 14o + 11tan'$.) PERTANNATE OF IRON.—This salt corresponds in composition with the best defined salts of iron; it consists of 1 atom of *peroxide of iron*, and $1\frac{1}{2}$ of *tannic acid*. It is important, as constituting the basis of common *writing ink**.

TANNATE OF LEAD ($pl + o$) + ($^{36}car + 18h + 24o$) or ($PL + tan'$) is formed by dropping a solution of nitrate or of acetate of lead into a solution of tannic acid, leaving the latter in excess. It is white and insoluble, and, if *neutral*, as it probably is, it consists of

					Berzelius.
Oxide of lead	. . . 1	. . . 112	. . . 34.2	. . . 34.21	
Tannic acid	. . . 1	. . . 213	. . . 65.8	. . . 65.79	
	1	325	100.0	100.00	

TANNATE OF ANTIMONY.—The compound of tannic acid with protoxide of antimony is thrown down from a solution of emetic tartar, in the form of an insoluble white gelatinous precipitate.

GENERAL CHARACTERS OF THE TANNATES.—The salts of the tannic acid are mostly of difficult solubility; those which are soluble do not precipitate gelatin except an acid be added. With the white oxides the pure tannates are white; with the coloured oxides, variously coloured. Infusion of galls, or a solution of tannic acid, are often used as reagents, indicating, by the colour of the produced precipitate, the nature of several of the oxides. The test should be applied to neutral solutions, for the effect is modified by the presence of free acids.

In the following Table of these precipitates by *infusion of galls*, the first column contains my own results, the second those given by Dumas:—

* In making good *Writing Ink*, the great object is to regulate the proportion of sulphate of iron to the galls. If it be in excess, although the ink may at first appear black, it becomes subsequently brown and yellow. Hence, some time should elapse before ink is used after the ingredients are put together, in order to be tested from time to time, and the combinations perfectly regulated. Gum is added to retain the colouring matter in suspension, to prevent too great fluidity in the writing, and to protect the vegetable matter from decomposition. Logwood, and other vegetable astringents, have been tried for atramental purposes, but do not yield a permanent ink.

An excellent ink is obtained as follows; but, if the paper has been made from inferior rags, bleached by an excess of chlorine, ink, however good, will be ultimately discoloured.

Aleppo galls 6 oz., sulphate of iron 4 oz., gum-arabic 4 oz., water 6 pints. Boil the galls in the water, then add the other ingredients, and keep the whole in a wooden or glass vessel, occasionally shaken. In two months, strain, and pour off the ink into glass bottles, to be well corked. To prevent mould, add one grain of corrosive sublimate, or three drops of kréosote to each pint of ink. Sulphate of copper is occasionally added to ink, but is rather injurious than otherwise.

A *blue ink*, or *writing fluid*, has lately been introduced: I am not acquainted with its composition, but the colouring matter is said to be sulphate of indigo and tannogallate of iron. Mr. Stephens has also patented a blue ink, the colouring matter of which is Prussian-blue dissolved in water by means of oxalic acid.

TABLE OF METALLIC PRECIPITATES

BY A STRONG INFUSION OF GALLS.

METAL.	SOLUTION.	PRECIPITATE.	
MANGANESE	Neutral protohydrochlorate	Dirty-yellow	0
IRON. . .	Neutral protosulphate	Purple tint	0
Ditto . .	Persulphate	Black	Blue-black
ZINC. . .	Chloride	Dirty-yellow	0
TIN . . .	Acid protochloride	Straw colour	Yellowish
Ditto . .	Acid perchloride	Fawn colour	Ditto
CADMIUM .	Chloride	?	0
COPPER . .	Protochloride	Yellow-brown	?
Ditto . .	Nitrate	Green	Gray
LEAD . . .	Nitrate	Dingy-yellow	White
ANTIMONY .	Tartrate of antimony and potassa	Straw colour	White
BISMUTH .	Tartrate of bismuth and potassa	Yellow, and copious	Orange
COBALT . .	Chloride	0	Yellow-white
URANIUM .	Sulphate	Dark-brown	Reddish-brown
TITANIUM .	Acid hydrochlorate	Brown-red	Blood-red
Ditto . .	Neutral sulphate	Blood-red	Ditto
CERIUM . .	Sulphate	Yellowish	Yellow
TELLURIUM	Chloride	Yellow	Yellow
ARSENIC .	White oxide	Little change	?
Ditto . .	Arsenic acid	0	?
MOLYBDENUM	Chloride	Brown	Brown
NICKEL .	Sulphate	Green	Yellow-green
MERCURY .	Acid protonitrate	Yellow	?
Ditto . .	Acid pernitrates	Yellow	?
Ditto . .	Corrosive sublimate	0	?
OSMIUM . .	Aqueous solution of oxide	Purple becoming blue	Bluish-purple
RHODIUM .			
PALLADIUM			
SILVER . .	Nitrate	Curdy and brown	Dirty-yellow
GOLD . . .	Chloride	Deep-brown	Brown
PLATINUM .	Chloride	Brownish-green	Dark-green

GALLIC ACID.—The researches of Pelouze have thrown much light on the nature and production of *gallic acid*, and have shown, that although it is found, in most cases, in vegetable products which contain tannin, it generally exists in small quantities only, and that in the usual mode of procuring it from *galls*, it is to be considered rather as a *product*, than an *educt*. Two methods of obtaining this acid have been resorted to; in the one, heat is applied so as to sublime it; in the other, it is procured by exposure of infusion of galls to air; in the former case the acid, as we shall immediately see, is modified; in the latter, it is produced by the action of oxygen on tannin, and it is in this way that the purest gallic acid may be obtained; as follows:—

Mix powdered galls into a thin paste with water, and expose it for four or five weeks, at a temperature between 60° and 70° , to the action of the air, observing to prevent its desiccation by the occasional addition of water: it swells and becomes mouldy, and, at the end of that period, contains a large proportion of *gallic acid*: the paste is dried by pressing out the *liquid*, (which holds scarcely any gallic acid in solution,) whilst the residue is boiled in water; the solution thus obtained is filtered whilst hot, and as it cools deposits gallic acid, which may at once be purified by boiling it with about 8 parts of water and a fifth of its weight of animal charcoal: the filtered solution now yields pure crystallized gallic acid as it cools.

In regard to the *theory* of this change, it has been observed above, that solution of tannin undergoes no change if excluded from oxygen; but if exposed to air, it slowly absorbs oxygen, giving out an equivalent volume of carbonic acid; so that, in a few weeks, the solution contains acicular crystals of gallic acid, formed at the expense of the tannin.

Gallic acid crystallizes, in combination with water, in long silky needles, which effloresce and become anhydrous when duly exposed to a temperature of about 250° . When perfectly free from tannin, it does not affect a solution of gelatin: its taste is slightly acid and styptic, and it requires about 100 parts of water for its solution: it is somewhat more soluble in ether, and considerably more so in alcohol. According to Pelouze (*Ann. de Ch. et Ph.*, liv. 337) the equivalent of *anhydrous gallic acid* is $85 = (7 \text{ car} + 3 \text{ h} + 5 \text{ o})$, or it consists of

				Pelouze.
Carbon	7	42	49.4	50.10
Hydrogen	3	3	3.5	3.64
Oxygen	5	40	47.1	46.26
Gallic acid	1	85	100.0	100.00

and the *crystallized gallic acid* consists of

				Pelouze.
Anhydrous gallic acid	1	85	90.4	90.55
Water	1	9	9.6	9.45
Crystallized gallic acid	1	94	100.0	100.00

PROPERTIES OF THE SALTS OF GALLIC ACID.—The *gallates* have been but little examined, and much confounded with the tannates. The gallates of *ammonia*, *potassa*, and *soda*, are soluble, and colourless out of the contact of air, but absorb oxygen, and become brown. In these cases,

and in the change which solution of gallic acid suffers, when exposed to air, Döbereiner states that *ulmin* is formed. The gallates of *lime*, *baryta*, and *strontia*, may be thrown down by the addition of gallic acid to the aqueous solutions of those earths, in the form of white powders, which redissolve in excess of the acid, and form silky prismatic crystals, unchanged by exposure to air. When these solutions, with excess of *base*, are exposed to air, they become discoloured.

With *persulphate of iron*, gallic acid produces a dark-blue precipitate, much more soluble than the pertannate of iron. This precipitate slowly redissolves in the supernatant solution: in a few days it becomes almost colourless, the sulphuric acid gradually resumes the greater part of the oxide of iron from the gallic acid, which separates in crystals, and the salt of iron contains a protoxide, in consequence of the decomposition of a portion of the gallic acid. These changes occur in a few minutes when the liquid is boiled. With solution of nitrate, or acetate of *lead*, gallic acid forms a permanent white precipitate, composed of

Oxide of lead	1	.	.	112	.	.	56.9
Gallic acid	.	1	.	85	.	.	43.1
Gallate of lead	1			197			100.0

ELLAGIC ACID.—This term, derived from the word *galle*, read backwards, has been applied by Braconnot (*Ann. de Ch. et Ph.*, ix. 181) to a substance produced along with gallic acid, by the exposure of moistened galls to air. Being insoluble in boiling water, it remains after the gallic acid has been extracted; and it may be dissolved out of the residue, by the action of a very weak solution of potassa, from which dilute hydrochloric acid throws it down in the form of a tawny powder, tasteless and almost insoluble. It does not decompose the alkaline carbonates, even at 212°. When a solution of *potassa* is dropped upon it, heat is produced, and it perfectly neutralizes the alkali: this salt, and that of *soda*, is soluble: but the *ellagate of ammonia* is, under all circumstances, nearly insoluble. Nitric acid forms a red solution with ellagic acid and changes it into oxalic acid. According to Pelouze, *anhydrous ellagic acid* is represented by the equivalent $76 = (7\text{ car} + 2\text{ h} + 4\text{ o})$, or

Carbon	7	.	.	42	.	.	55.3
Hydrogen	2	.	.	2	.	.	2.6
Oxygen	4	.	.	32	.	.	42.1
Ellagic acid	1			76			100.0

PYROGALLIC ACID.—This acid, first noticed by Deyeux (*Jour. de Ph.*, xlii. 416), has since been studied by Braconnot (*Ann. de Ch. et Ph.*, xlii. 206), and by Pelouze (*Ibid.*, liv. 337). It is, as its name imports, produced by the action of heat upon gallic acid, but a particular temperature is requisite for its formation, which Pelouze determined, by heating the retort containing the gallic acid in an oil bath, to be between 410° and 420°; a little above that heat no pyrogalllic acid is produced, but another distinct product, which has been called *metagallic acid*. The preparation, therefore, of pyrogalllic acid requires much care as to temperature; it is best produced by half-filling a small retort with gallic acid, and heating it through the medium of an oil-bath with an immersed thermo-

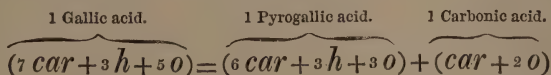
meter. It sublimes in the form of white and brilliant lamellar and anhydrous crystals, very soluble in water, alcohol, and ether, and slightly reddening litmus. Exposed to air, its aqueous solution gradually acquires colour, and in the course of some days, is entirely resolved into what appears to be *ulmin*. It fuses at 247° , and boils at 410° , yielding a colourless vapour of a slightly balsamic odour: at 480° it blackens, and is resolved into *metagallie acid* and water. Pyrogallie acid has been analyzed by Berzelius under the name of gallic acid, and also by Pelouze: their experiments indicate its formula to be $(6\text{ car} + 3\text{ h} + 3\text{ o})$, or

					Berzelius.	Pelouze.
Carbon	6	36	57.14	56.64	57.61	
Hydrogen	3	3	4.76	5.00	4.70	
Oxygen	3	24	38.10	38.36	37.69	
Pyrogallic acid	1	63	100.00	100.00	100.00	

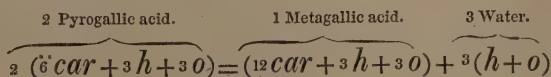
PYROGALLATES.—Ammonia, soda, and potassa, form soluble pyrogallates: that of potassa crystallizes in white rhomboidal tables. Pyrogallie acid produces no precipitate in lime, baryta, or strontia water. According to Braconnot it instantly reduces persulphate of iron to protosulphate, and the liquid acquires a reddish-brown tinge, without depositing any precipitate. If, instead of the free acid, a pyrogallate be used, or hydrated peroxide of iron, an intense blue precipitate falls. Protosulphate of iron produces an immediate blackening.

METAGALLIC ACID.—When tannic or gallic acid is rapidly heated up to 480° , carbonic acid and water are evolved, and, instead of a sublimate of pyrogallie acid, a black, shining, and tasteless substance is formed, insoluble in water, but readily soluble in liquid ammonia, potassa, and soda, and disengaging carbonic acid, with effervescence, from the soluble alkaline carbonates. Metagallate of potassa gives black precipitates with the salts of lime, baryta, strontia, magnesia, iron, zinc, copper, lead, and silver. The equivalent of this acid appears to be $99 = (12\text{ car} + 3\text{ h} + 3\text{ o})$. The acid, at first formed, contains 1 equivalent of water.

ATOMIC RELATIONS OF THE PRECEDING ACIDS.—The decomposition of gallic acid, at the temperature of 420° , is such, that 1 equivalent yields 1 of pyrogallie acid and 1 of carbonic acid; for



and, at the temperature of 480° , 2 atoms of pyrogallie acid yield 1 atom of metagallie acid and 3 of water; for



CATECHUIC ACID is the name given to an acid obtained from catechu, and which, by the action of potassa and exposure to oxygen, is converted into *Japonic acid* and *Rubinic acid*. (THOMSON, *Organic Chem.*, 113, and Pogg., xxxix. 161.)

§ X. COLORIFIC EXTRACTIVE. COLOURING MATTER.

THE *colouring matters* of vegetables which are soluble in water, generally partake more or less of the chemical properties of *extractive*, and like that principle, are capable of being combined with, and fixed, or rendered permanent by certain bases or oxides, which, in reference to this particular case, are often termed *mordants*.

When a solution of *brown extractive matter*, for instance, is mixed with a solution of certain salts of iron, lead, or aluminum, and an alkali is added to the mixture, the metallic oxide falls in chemical combination with the extractive matter, so that the supernatant liquor remains colourless. The same thing happens with other colorific extracts; an infusion of madder, for example, when mixed with a solution of alum, and decomposed by an alkali, furnishes a *red* precipitate, and if the alumina be in excess, the residuary solution is perfectly colourless. Other coloured solutions present the same phenomena, and the coloured precipitates are, in such cases, often termed *lakes*, especially when of a red, pink, or purple tint. In these cases, an attraction is shown to exist between the *metallic oxide* and the *colouring matter*, and it is often the means of conferring a degree of permanence and insolubility on the latter, and modifying its hue. It has already been stated that the various forms of *lignin*, or vegetable fibre, possess a similar attraction for certain oxides: accordingly, if a piece of linen or calico be steeped in a proper solution of such oxide, a combination of the fibre and the oxide will first take place; and then, the fibre thus prepared, if immersed in a solution of colouring extract, will combine with it, and the colour thus become fixed upon the stuff. This, in a few words, is the *theory* of the art of dyeing, with the greater number of vegetable colours, which, though in themselves fugitive, and unsusceptible of combination with the linen, cotton, or other material to be dyed, are rendered, to a greater or less extent, fixed and permanent, by the joint attraction of the base or mordant for the fibre and for the colour*.

* The art of dyeing and calico-printing has been the subject of several separate works, to which the reader is referred for details. The following are a few of the principal points which bear upon the chemistry of the processes.

In the first place, the goods require to be thoroughly cleansed from all foreign matters and colours, which is effected by washing and *bleaching*. Warm water is at first liberally applied to remove the filth acquired in weaving; the goods, if linen or cotton, are then *bowked*, or boiled with a very weak solution of caustic potassa, washed in large quantities of water, and spread out upon the grass so as to be exposed freely to the joint agencies of light, air, and moisture; this part of the operation, which is tedious, may be much curtailed, or even superseded, by the careful application

of a weak solution of chloride of lime. The bowking and exposure are alternately repeated as often as necessary; and lastly, the goods are immersed in water slightly acidulated by sulphuric acid, again thoroughly washed, and dried. By these operations the texture of the stuffs is always more or less impaired, especially when chloride of lime is used. In respect to the *theory* of the operation of bleaching, it appears probable, that, in the necessary exposure to water, air, and light, or their substitute *chlorine*, *nascent oxygen* is developed, and is the destroyer of those portions of colouring matter which are most obstinately retained. With respect to the nature of the materials or fibre to be dyed, it is found that different substances not only possess very different attractions for dye-stuffs, but they absorb

There are other circumstances in which the different colouring principles resemble each other, and which will be apparent in the following

the colouring matter in very different proportions. Wool appears in this respect to have the strongest attraction for colouring substances; silk comes next to it; then cotton; and lastly, hemp and flax. The simple operation of dyeing is generally performed upon *animal fibre*, such as wool and silk, whilst the more refined operation of printing in patterns and devices of various colours, is chiefly, though by no means exclusively, conducted upon *cotton*, or as it is usually termed, *calico*. It has been above stated, that very few colours are of such a nature as to combine with the fibre without some *intermedium*: where this is the case, they constitute what have been termed *substantive colours*: but they generally require the intervention of a *base* or *mordant*, and are called *adjective colours*. The mordants which are most frequently resorted to, are, as has already been remarked, salts of alumina, iron, and tin. The substance to be dyed is first impregnated with the mordant, and then passed through a solution of the colouring matter, which is thus fixed in the fibre, and its tint is often modified or exalted by the operation. That a considerable portion of the mordant is retained in the fibre of the calico or cloth dyed, has been proved by the experiments of Dr. Ure. He found that 100 parts of the ashes of Turkey red calico (dyed by an alum mordant) afforded between 16 and 17 parts of alumina; whereas the ashes of white and washed calico only afforded a trace of that earth. (See two papers, by Dr. Ure, on the incinerated ashes of cotton-wool and calico dyed by the Turkey red process. *Quart. Journ.*, xxi. 28—297.)

Calico-printing, which is a more refined and difficult branch of the art, is a species of topical dyeing. In this process *adjective colours* are almost always employed. The mordants, the principal of which are acetate of alumina, and acetate of iron, are first applied to the calico by means of wooden blocks or copper-plates, or cylinders, upon which the requisite patterns are engraved. The stuff is then passed through the colouring bath, and afterwards exposed on the bleaching-ground, or washed. The colour flies from those parts which have not received the mordant, and is permanently re-

tained on those parts only, to which the mordant has been applied: variety of colours is produced by employing various mordants, and different colouring materials, and by using them in various states of dilution and combination.

White spots upon a dark ground are sometimes produced by covering the parts with wax, pipe-clay, or other materials, which prevent the contact of the colour; or citric acid, thickened with gum, is applied like a mordant with the block or plate, and prevents the retention of the colour. Sometimes the colour is discharged in places, by the application of chlorine, a process well illustrated in what are called *Bandana* handkerchiefs, of which an account will be found, by Dr. Ure, in the fifteenth volume of the *Quarterly Journal*. There is also an interesting series of papers on the subject of calico-printing, in the *Records of Science*, edited by Dr. Thomson, from which some idea may be formed of the refined and complex chemical operations which have been successfully applied to the perfection of that beautiful art.

Besides the vegetable colours which are enumerated in the text, and very many others which are occasionally resorted to, and their various *mixtures*, by which an infinite variety of *compound colours* are obtained, *metallic colours* are constantly employed both in dyeing and calico-printing. These colours are not only infinitely various, but often admirably adapted to the processes of the art. Thus, the attraction of oxide of iron for different fibres, which renders it of such importance as a mordant, enables the dyer and printer to avail themselves of *Prussian blue*: and with other metallic mordants, such as oxides of lead, copper, &c., the ferrocyannuret of potassium, iodide of potassium, chromate of potassa, arsenio-sulphurets, and various other salts, become the sources of a great variety of beautiful colours.

Instead of first applying the mordant, and afterwards the colouring material, they are occasionally both printed together, but in these cases, particular management is requisite in the selection of the substances employed, and in the mode of their application: when this method is resorted to, the colour is often *fixed* by the application of steam at 212°.

account of a few of the most important of them: they are generally impaired or destroyed by the continuous action of light, especially if aided by moisture and a certain temperature: they are also destroyed by chlorine, and by peroxide of hydrogen, and some other compounds in which oxygen is very loosely retained, and also by a few of the acids: among these, sulphurous acid is the most remarkable. The art of *bleaching* depends upon these properties, by which various colouring matters are decomposed and destroyed, or converted into colourless compounds.

As far as their use in the arts is concerned, the *red*, *yellow*, and *blue* colouring matters are the most important; and from these, the following may be selected for more particular description, on account of their applications and chemical properties.

A. REDS.—1. MADDER.—The plant which furnishes this valuable dye stuff, (*Rubia tinctorum*, Linn.,) is common in the south of Europe, and in many parts of the Levant, and is largely cultivated in Holland: it grows to about three feet in height, and has a long spreading fibrous root, which is the part used in dyeing. It is carefully dried and cleaned, and afterwards ground into a coarse powder, which is of a dingy red or orange colour, and very apt to be deteriorated by moisture. The Levantine madder, called *ligari*, *allizari*, *azale*, has a finer colour than the Dutch, but the latter is more carefully prepared and dried. When cold water is digested upon madder, it dissolves gum, sugar, *yellow* extractive, and free malic acid: the residue, boiled in water, with a small addition of carbonate of soda, yields a dark red decoction, from which sulphuric acid throws down the red colouring matter: it may be purified by drying it upon blotting-paper, and solution in alcohol: to the filtered tincture a little carbonate of potassa is added to separate sulphuric acid, and when poured off from the precipitated sulphate of potassa and evaporated, it leaves the colouring principle in the form of a confused crystalline mass. (KUHLMANN, *Ann. de Ch. et Ph.*, xxiv. 225.) From this colouring matter, Colin and Robiquet have obtained a crystallizable substance, which they call *Alizarine*. (*Ann de Ch. et Ph.*, xxxiv. 225.) There are several processes for its preparation, the simplest of which appears to be the following, suggested by Zenneck (*Quart. Jour.*, N. S., v. 198):—Digest 10 parts of finely-powdered madder with 4 parts of ether, in a close flask: the clear solution is to be distilled until the residue is thick like a syrup, and then dried upon plates in the open air, powdered, and sublimed. The sublimation is to be effected in a watch-glass, or a metallic capsule, covered by a very low cone, on which the vapours are to be condensed; the layer of matter to be sublimed must be thin, and the distance through which the vapours have to pass as small as possible; a little cotton should be placed at the orifice in the summit of the condensing cone, and the heat applied moderate, especially at the commencement.

Alizarine, well sublimed, is in very brilliant, diaphanous, yellowish red, acicular, quadrangular crystals; they are soft, flexible, heavier than water, have an acid taste, soften when heated, sublime at the temperature of boiling oil, and then occasion a peculiar aromatic odour. It is nearly insoluble in cold water. At common temperature, 1 part dissolves in 210 of alcohol, and in 160 of ether. It combines with and dissolves in

alkalis, forming violet solutions; and, in fact, has all the properties of an acid. It even passes to the positive pole of the voltaic pile; and when boiled with metallic zinc, causes its oxidation, and then unites with it; 100 parts combine with and saturate 350 parts of oxide of lead: so that it has a greater saturating power than oxalic acid. Its composition per cent. is given as 18 carbon, 20 hydrogen, and 62 oxygen.

2. SAFFLOWER is the term given to the petals of the *Carthamus tinctorius*, or *Bastard saffron*: it is cultivated in Spain, and in many parts of the Levant, whence it is chiefly imported; but on account of its price it is seldom used, except to give the finishing hue to some silks, and in the preparation of the article called *rouge*. Safflower contains two colouring matters, a *yellow* and a *red*, and as the former spoils the tint of the latter, it is removed by washing the safflower in a linen bag, in a stream of pure cold water: the residue yields the *red* colour, by digestion in a cold solution of carbonate of soda, from which it may be precipitated by a weak acid, lemon-juice being preferred. Good safflower affords about 5 per cent. of this product, which, according to Döbereiner, is a peculiar acid, (*carthamine*, *carthamic acid*.) It is insoluble in pure and in acidulated water, and in oils; sparingly soluble in alcohol and ether; yields a yellow solution with alkalis; and with soda a colourless crystalline salt, which acids instantly redden. This colouring matter is easily bleached: when mixed with talc in fine powder, it forms common *rouge*.

3. NICARAGUA, PEACH, BRAZIL, FERNAMBOUC, AND SAPAN WOOD.—These are the woods of certain species of *Cæsalpina*: they give out their colouring matter to water: it is of different tints of red and pink, becoming yellow by acids, and blue or purple by alkalis, and easily bleached. It is soluble in alcohol. The infusion in weak citric or phosphoric acid is a good yellow dye. Various tints of violet, red, and purple, may be obtained by the action of acids and alkalis. The salts of iron render it deep blue. It is the colouring matter of *red ink*, which is usually made by boiling about two ounces of Brazil wood in a pint of water for a quarter of an hour, and adding a little gum and alum. (The finest *red ink* is that procured by digesting cochineal in a very weak solution of ammonia.) Nitrohydrochlorate of tin carries down the greater part of the colour of infusion of Brazil wood, and alumina forms with it variously tinted *lakes*. The infusion of peach wood is very well adapted for extemporaneous illustrations of the art of dyeing and calico-printing. Besides colouring matter, the aqueous infusion of Brazil wood contains free acetic acid, tannin, and acetates of potassa and lime, with a trace of volatile oil.

4. LOGWOOD. CAMPEACHY WOOD.—This is the wood of the *Hæmatoxylon campechianum*, a large tree which grows in various parts of the West Indies, and especially on the Bay of Campeachy, and along the American continent. It is largely imported from Jamaica, as a dye stuff. It has a sweetish astringent taste, and a peculiar odour: an extract prepared from it is used in medicine. It contains, according to Chevreul, a peculiar colouring-principle, which he has termed *Hematin*, and which may be obtained as follows.

On the watery extract of logwood, digest alcohol for a day, filter the solution, evaporate, add a little water, evaporate gently again, and then leave the liquid at rest. Hematin is deposited in small crystals, which, after washing with alcohol, are brilliant, and of a reddish-white colour. Their taste is bitter, and astringent.

Hematin forms an orange-red solution with boiling water, becoming yellow as it cools, but recovering, when heated, its former hue. Alkali converts it first to purple, then to violet, and lastly, to brown: in which state it seems to be decomposed. Metallic oxides unite with it, forming blue compounds. Gelatin throws down reddish flocculi. Protohydrochlorate of tin renders it lilac.

Logwood shavings yield their colour to water and alcohol: the latter extracts it more readily than water. The colour of its dyes is red, inclining to violet or purple. Its aqueous decoction, left to itself, becomes yellowish, and at length black. Acids turn it yellow; alkalis deepen its colour, and give it a purple hue. Stuffs would take only a slight and fading colour from decoction of logwood, if they were not previously prepared with aluminous mordants. A blue colour may be obtained from it, by the addition of verdigris; but the great consumption of logwood is for blacks, which are obtained by alum and iron bases, and of any requisite degree of intensity. (See also upon the subject of the colouring principle of logwood, GOLPIER-BESSEYRE, *Ann. de Ch. et Ph.*, LXX. 272.)

5. RED SANDAL, or SAUNDERS WOOD, is the produce of the *Pterocarpus santalinus*, and contains a deep red colouring matter, which is insoluble in pure water, but which may be extracted by alcohol and by alkalis. When its alcoholic solution is evaporated, it remains in the form of a red resin, fusible at 212° , and soluble in ammonia, or carbonate of ammonia, from which solutions it may be precipitated by hydrochloric acid: it is also soluble in acetic acid. Fine purple precipitates are thrown down in its alcoholic solution by protochloride of tin and by subacetate of lead, deep violet by sulphate of iron, scarlet by corrosive sublimate, and brown by nitrate of silver. Ether dissolves the colouring matter of this wood more perfectly than alcohol, and water throws it down from the latter. The acetic solution of it causes an orange-coloured precipitate with gelatine. (PELLETIER, *Jour. de Phys.*, LXXIX. 268.)

6. ALKANET is the root of the *Anchusa tinctoria*, a species of bugloss, which is a native of the warmer parts of Europe, and cultivated in our gardens. The greatest quantities are raised in Germany and France. This root imparts a deep red colour to alcohol, oils, wax, and all unctuous substances. Its colouring principle (*alcannin* or *anchusic acid*, a fatty acid, see PELLETIER, *Jour. de Phys.*, LXXIX. 278, and JOHN, *Chem. Schrift.*, iv.) may be obtained by the evaporation of its ethereal tincture, or by precipitating its solution in carbonated alkalis by a dilute acid. It is insoluble in water, but soluble in alcohol and ether, and in the fat and volatile oils, to which it imparts a fine red. Its alcoholic solution is imperfectly decomposed by water. The alkalis render it blue, and the acids restore its red. It is precipitated crimson by solution of protochloride of tin; blue, by subacetate of lead; dark violet, by the salts of iron; and pale red, by corrosive sublimate.

The principal use of alkanet root is, that of colouring oils, unguents, and lip salves. Wax tinged with it and applied on warm marble, stains it of a flesh colour which sinks deep into the stone; the spirituous tincture gives it a deep red stain.

As the colour of this root is confined to the bark, and the small roots have more bark in proportion to their bulk than the larger ones, these also afford most colour.

7. ARCHIL. ROCELLA. ORSELLE.—This is a whitish lichen, growing upon rocks in the Canary and Cape Verd Islands, which yields a purple tincture, fugitive, but extremely beautiful. This weed is imported as it is gathered: those who prepare it for the dyer, grind it so as to bruise, but not reduce it into powder, and then moisten it occasionally with urine mixed with quick-lime: in a few days it acquires a blue colour; in the first state it is called *archil*, in the latter *lacmus* or *litmus*. The term *Cudbear* is also often applied to this dye-stuff, a term said to be derived from the name of its discoverer, *Cuthbert Gordon*.

The chief use made of archil is for giving a bloom to other colours, which is effected by passing the dyed cloth or silk through hot water slightly impregnated with it. This bloom fades upon exposure to air: solution of tin renders it more durable, and its colour is at the same time changed toward a scarlet. Prepared archil gives out its colour to water, alkalis, and alcohol*.

Litmus is used as a *test*, either by staining paper with it, or by infusing it in water, when it is very commonly called *tincture of turnsole*. The persons by whom this article was prepared, formerly gave it the name of turnsole, pretending that it was extracted from the turnsole, *Heliotropium tricoctum*, in order to keep its true source a secret. The light of the sun does, however, turn it red, even in close vessels. This tincture may be made with spirit instead of water. The tincture, or paper stained with it, is presently turned red by acids: and if it be first reddened by a small quantity of vinegar, or some weak acid, its blue colour will be restored by an alkali.

8. CHICA RED is the colouring matter obtained from a species of *Bignonia*, and used by the American Indians to colour the skin. It is soluble in water, alcohol, and ether. (BOUSSINGAULT, *Ann. de Ch. et Ph.*, xxvii. 315.)

* It was the colouring matter formerly used for tinging the spirit in thermometer tubes, but was very liable to fade. The Abbé Nollet observes, (in the *French Memoirs* for the year 1742,) that the *colourless* spirit, upon breaking the tube, soon resumes its colour, and this for a number of times successively; that a watery tincture of archil, included in the tubes of thermometers, lost its colour in three days; and that in an open deep vessel, it became colourless at the bottom, while the upper part retained its colour. A solution of archil

in water, applied on cold marble, stains it of a beautiful violet or purplish-blue colour, far more durable than the colour which it communicates to other bodies. M. du Fay says, he has seen pieces of marble stained with it, which in two years had suffered no sensible change. It sinks deep into the marble, sometimes above an inch, and at the same time spreads upon the surface, unless the edges be bounded by wax or some similar substance. It is said to make the marble somewhat more brittle, but this is probably erroneous,

9. ANIMAL REDS. COCHINEAL RED; LAC RED; KERMES.—These substances are principally used in conferring upon woollen cloth the colour commonly called *scarlet*. *Cochineal* is a small insect brought from Mexico, where it is found upon different species of the *Cactus*. The nature of this colouring matter has been investigated by MM. Pelletier and Caven-
 tou; it is united in the insect with a peculiar animal matter, fat, and some saline substances; they separated it by exposing a strong alcoholic tincture of cochineal to spontaneous evaporation; it deposited a crystal-
 line matter, which was redissolved in alcohol, and the solution mixed with its bulk of sulphuric ether; this caused it in a few days to deposit the pure colouring principle, which they call *Carminium*: Dr. John has proposed for it the term *Coccinellin*. This substance is fusible at about 120°, very soluble in water, less so in alcohol, and insoluble in ether; the acids change its colour from purple to pale red or yellow: the alkalis render it violet; and its colour is impaired by most saline solutions. It readily combines with alumina, forming a beautiful *lake* or *carmine*. He obtained from 100 parts of cochineal, 50 of coccinellin, 24·5 gelatine and mucous matter, 10 waxy fat, 14 membrane, 1·5 saline matters.

The colouring matter of cochineal is fixed upon wool by nitrohydrochlo-
 rate of tin and tartar, by which *scarlets* are produced, and alum changes the scarlet to crimson. Cotton and linen are very rarely dyed with cochineal, for, independent of its great expense, the colours are little superior to those given by madder.

LAC is a substance formed by an insect, and deposited on different species of trees, chiefly in the East Indies. The various kinds of lac distinguished in commerce, are *stick lac*, which is the substance in its natural state, investing the small twigs of the tree; *seed lac*, which is the same broken off; and which, when melted, is called *shell lac*. These substances have been examined by Mr. Hatchett. The following table exhibits their component parts. (*Phil. Trans.*, 1804.)

	Stick lac.	Seed lac.	Shell lac.
Resin	68	88·5	90·9
Colouring matter	10	2·5	0·5
Wax	6	4·5	4·0
Gluten	5·5	2·0	2·8
Foreign bodies	6·5	—	—
Loss	4·0	2·5	1·8
	100·0	100·0	100·0

Dr. John has announced the presence of a peculiar acid in stick lac, which he has called *laccic acid*. The lac was digested in water, the solution evaporated, and the residue digested in alcohol: the alcoholic solution was evaporated to dryness, and its residue digested in ether. The evaporation of the etheric solution leaves a yellow matter, which, being again dissolved in alcohol, and the solution mixed with water, deposits a little resin, and leaves laccic acid in solution, which, upon the addition of acetate of lead, gives a precipitate of *laccate of lead*; the latter compound, by cautious decomposition by sulphuric acid, affords the laccic acid.

Laccic acid is crystallizable, of a yellow colour, a sour taste, and soluble in water, alcohol, and ether. With potassa, soda, and lime, it forms

deliquescent soluble *laccates*; with lead and mercury it produces white insoluble compounds; it occasions no precipitate in the nitrates of baryta and silver. (THOMSON'S *System*, ii. 177. Dr. Pearson obtained a peculiar acid from a substance called *white lac*, from Madras, which he has also called *laccic acid*. *Phil. Trans.*, 1794.) There are two preparations of the *colouring matter* of *lac* imported from India, under the names of *lac lake* and *lac dye*. The latter is by far the most valuable, and is extensively employed in dyeing scarlet as a substitute for cochineal. It is to be regretted that the preparation of this valuable dye stuff is not more carefully attended to.

KERMES, or the *Coccus ilicis*, a small insect found in many parts of Asia, and in the south of Europe; and the *Coccus Polonicus*, found adhering to the roots of *Polygonum*, and employed as a dye stuff in Poland and in Turkey, also contain a red colouring principle. The scarlets and crimsons which they produce, are said to be brilliant and permanent. Tartar and solutions of tin are used to produce scarlet; and aluminous bases, and soap, for crimson.

B. YELLOWS.—1. QUERCITRON BARK.—This is the bark of the *Quercus tinctoria*, or *Quercus nigra* of North America: it was first introduced into England by Dr. Bancroft (*Philosophy of Permanent Colours*, London, 1813), and is now one of our most important dyeing-materials. Its colouring principle, which amounts to about 8 per cent., may be extracted by water; a quantity of tannin is at the same time taken up, which would be prejudicial, and therefore glue, bladder, or some similar gelatinous membrane, is added to the infusion, by which the tannin is abstracted. The yellow colorific extract may then be precipitated in combination with alumina, or with oxide of tin. With the salts of iron it gives a variety of olive and drab tints, dependent upon the presence of more or less tannin, and the degree of dilution.

2. FUSTIC.—This is the wood of the *Morus tinctoria*, a large tree which grows in many parts of the West Indies, and on the American continent. It yields 9·1 colouring matter with some gallic acid, 4 tannin, 2 gum, 9 resin, 74 lignin. (GEORGE, as quoted by Berzelius.) Its decoction is orange-coloured, and is improved as a yellow dye by the addition of gelatin. Alkalis deepen its colour, and acids render it paler. Acetate of lead and protochloride of tin give deep-yellow precipitates with it, the tint of which is brightened by tartar and alum.

WELD. (*Reseda luteola*.)—This is a slender plant, growing to the height of about three feet, and cultivated for dyers. When ripe it is cut and dried. Its decoction is of different shades of yellow, according to its strength. Alkalis deepen its tint, and acids render it paler. Alum, tartar, and solutions of tin, brighten it, and give it more or less of a deep-lemmon tint. *Dyer's Broom* (the *Genista tinctoria*, Linn.), and the American *Golden Rod* (*Solidago canadensis*), also contain a yellow extractive, from which yellow dyes are obtained. A water colour, called *weld-yellow*, is much used by paper-hanging manufacturers. It is the colouring matter of weld precipitated with an earthy base. It is prepared as follows:—Into a copper vessel put four pounds of fine washed whiting, and

as much soft water, and boil them together, stirring them with a deal stick, till the whole forms a smooth mixture: then add gradually twelve ounces of powdered alum, still stirring, till the effervescence ceases, and the whole is well mixed. Into another copper put any quantity of weld, with the roots uppermost; pour in soft water enough to cover every part containing seed; let it boil, but not more than a quarter of an hour; take out the weld, and set it to drain; and pass the whole of the liquor through flannel. To the hot mixture of chalk, alum, and water, add as much of this decoction as will produce a good colour, keep it on the fire till it boils, and then pour it out into a wooden or earthen vessel. The next day the liquor may be decanted, and the colour dried on chalk. (URE's *Dictionary*.)

4. ANNOTTO. (*Roucou. Orlean.*)—This article is procured from the seeds of a large tree, the *Bixa orellana*. When ripe, they are bruised, soaked, and beaten into a pulp, which, after due fermentation, is boiled with water, during which it throws up a scum, which is collected, dried, and made into cakes or rolls, of two or three pounds weight: in this state it comes into our market from Cayenne, and other parts of America. Its colouring matter is soluble in water, and more so in alcohol and alkaline liquors: it has a disagreeable smell and taste. It is a powerful dye, and is used also to colour various varnishes, and to give the deep-orange tint to Cheshire cheese. (BOUSSINGAULT, *Ann. de Ch. et Ph.*, xxviii. 440.)

5. TURMERIC is the root of the *Curcuma longa*. It yields a yellow colour, slightly to water, but very abundantly to alcohol, and to alkaline solutions: the latter impart to it a deep-brown tint, hence its use in the laboratory as a *test*. Acids, with some few exceptions (such as the boracic, and hydrochloric acid gas, which tinge turmeric paper brown), render it bright-yellow. It is much used in cookery to give yellow tints, and is an ingredient in *curry powder*.

6. SAFFRON.—The stigmata of the *Crocus sativus*, form the article known in commerce under this name. Bouillon la Grange and Vogel have given the term *Polychroite* to its colouring principle (*Ann. de Ch.*, LXXX. 198), from the variety of colours which it produces under the influence of various reagents. But Henry (of Paris) has shown that polychroite is a compound of extractive and essential oil, and that the extract alone is not possessed of any important peculiarities.

C. BLUES.—The blue colouring-matter of plants is chiefly resident in the petals of flowers, but the fruits and other parts which contain purple or red juices, may generally be rendered blue by the action of an alkali, or other base, which saturates the acids that are present; so that the original colouring principle often appears in these cases to possess a blue colour, reddened by the action of one or more of the vegetable acids.

The colouring matter of most *flowers* is extremely fugitive, and is generally much changed by mere exsiccation. They usually communicate their colour to water: the infusion of *blue* flowers is generally reddened by acids, and changed to green or yellow by alkalis; that of *yellow* flowers is made paler by acids, and alkalis render it brown: the *red* infusion of many flowers is exalted in tint by acids, and changed to purple, and in

some instances to green, by alkalis; so that probably one and the same principle gives colour to several of the blue and red flowers, but the presence of acid in the latter produces the red; the petals of the red rose, triturated with a little carbonate of lime and water, give a blue liquor; alkalis render it green, and acids restore the red.

A colouring matter, analogous to that of the violet, exists in the petals of red clover, in the red tips of those of the common daisy, of the blue hyacinth, the holyhock, lavender, in the inner leaves of the artichoke, and in numerous other flowers; reddened by an acid, it colours the skin of several plums, and the petals of the scarlet geranium and pomegranate. Some flowers which are red become blue by merely bruising them; this is also the case with the colouring matter of red cabbage leaves, and of the rind of the long radish. Mr. Smithson has suggested that the reddening acid is in these cases the carbonic, which escapes on the rupture of the vessels which enclose it.

The petals of the common *corn poppy*, rubbed upon paper, give a purple stain, little altered by ammonia or carbonate of soda, but made green by caustic potassa. The infusion of poppy-petals in very dilute hydrochloric acid, is florid red; chalk added, renders it of the colour of port wine; carbonate of soda in excess gives the same colour, but excess of potassa changes it to green and yellow.

The colouring matter of *fruits* seems, in most cases, to bear a strong resemblance to that of flowers. The red juice of the mulberry was found to exhibit the same characters as the colouring principle of the wild poppy; carbonated alkalis render it blue, but caustic potassa changes it to green and yellow: the juice of red currants, cherries, elder-berries, and privet-berries, and the skin of the buckthorn-berry, appear to contain a similar colouring principle. The unripe berries of the buckthorn furnish a juice, which, when inspissated, is known under the name of *sap-green*. It is soluble in water, and rendered yellow by carbonate of soda and caustic potassa; the acids redden it, and carbonate of lime restores it to green, which is therefore probably the proper colour of the substance. (SMITHSON, *Phil. Trans.*, 1818.) Black currants, the common blackberries, the ripe berries of the Portugal laurel, and several other common fruits and berries, contain similar colouring matters.

INDIGO.—The most important blue colouring matter is the substance called *Indigo*; it is evidently a vegetable principle *sui generis*, but from its value as a dye-stuff, I shall place it among the *colorific extractive principles*; indeed, in its original state, as it exists in the sap of the plants whence it is obtained, it appears to be as nearly allied to extractive, as to any of the other proximate principles; but as we shall presently find, its character as a proximate principle, and its ultimate or elementary composition, are distinct and peculiar.

Indigo is obtained chiefly from different species of *Indigofera*, an American and Asiatic plant, cultivated as a source of this article; it is also obtained from the *Nerium tinctorium*; and from some species of *Isatis*, or *woad*. The dye is extracted either from the fresh or dried plant, by suffering it to ferment with water, during which it undergoes chemical changes, which ultimately cause its deposition in the form of a

blue feculent deposit, which is collected and dried. In regard to the details of its manufacture, two papers will be found in the *Quarterly Journal of Science* (vols. v. and vi., *new series*, pp. 296 and 265), in which the principal steps of the operation, and the probable nature of the results, are explained. The general characters of indigo, as it is found in commerce, are the following: it occurs in square cakes, or cubical masses of a deep-blue colour, and generally containing about 50 per cent. of pure colouring matter, which is perfectly insoluble in water; when heated to between 500° and 600° , it affords a sublimate in the form of a blue smoke, which, on condensation, forms acicular crystals, amounting in weight to 18 or 20 per cent. of the original indigo. It is soluble in concentrated sulphuric acid. This solution is usually called *Saxon*, or *liquid blue*, and is used as a substantive colour for dyeing cloth and silk. Substances which powerfully attract oxygen render indigo green, and by exposure to air, it again acquires a blue colour. In this green state, indigo is soluble in the alkalis, and the solution is commonly employed for dyeing calico. A bath for this purpose may be made by mixing 1 part of indigo, 2 parts of sulphate of iron, and 2 of lime, in a sufficient quantity of water: in this case, the sulphate of iron is decomposed by a portion of the lime, and the protoxide of iron thus produced becomes peroxidized at the expense of the indigo, which is rendered green and soluble in the alkaline liquor; cotton steeped in this solution acquires a green colour, which, by exposure to air, and washing in water acidulated with sulphuric acid, becomes a permanent blue. A little iron or zinc thrown into diluted sulphate of indigo changes or destroys the colour, in consequence of the evolution of hydrogen; the colour is also quickly impaired and destroyed by chlorine.

The analysis of indigo, to ascertain the proportion of *colouring matter*, which varies much in different samples, may be performed by the successive action of water, alcohol, and hydrochloric acid. (CHEVREUL, *Ann. de Ch.*, LXVI. 20.) 100 parts of Guatemala indigo, thus treated, afforded

To Water . . .	{	Green matter combined with ammonia	} 12	
		Deoxidized indigo		
		Extract		
		Gum		
To Alcohol . .	{	Green matter	} 30	
		Resin		
		A trace of indigo		
To Hydrochloric Acid	{	Red resin	} 6	
		Carbonate of lime		2
		Oxide of iron		} 2
		Alumina		
Residue	{	Silica	} 3	
		Pure indigo		45
			100	

Indigo has also been subjected to an interesting series of experiments by Berzelius (*Ann. de Ch. et Ph.*, Nov. et Dec., 1827), who found its usual constituents to be four distinct substances: viz., 1. gluten; 2. a peculiar brown substance, apparently resembling extract; 3. a red substance, which gives a white sublimate when heated in close vessels;

4. indigo blue. 1. The substance which Berzelius terms *Gluten*, is soluble both in alcohol and water, and was obtained by digesting powdered indigo in dilute sulphuric acid, neutralizing the solution by chalk, filtering, evaporating to dryness, and digesting the residue in alcohol. 2. The *Brown matter* was taken up from the indigo (freed as above from gluten) by potassa, and by sulphuric acid precipitated. 3. Upon the indigo, thus purified by dilute acid and by the action of solution of potassa, strong alcohol was digested, which took up a *red substance*, insoluble in water and alkalis, soluble in concentrated sulphuric acid, and in nitric acid, and which, when heated in vacuo, yielded a gray crystalline sublimate. 4. The substance remaining after the action of the above solvents is the real colouring matter of the indigo, or *indigo blue*, and is that which forms the purple vapour and sublimate above alluded to. It forms a deep-blue solution of great intensity with sulphuric acid, and especially with the fuming and partly anhydrous acid (Nordhausen acid), and is, in fact, the principal ingredient in the sulphuric dyeing-liquor already mentioned.

The action of sulphuric acid upon indigo has been investigated by Mr. Crum. (*Ann. of Phil.*, N. S., v. 81.) The concentrated acid does not merely dissolve it, but, in the course of twenty-four hours, alters its properties; it at first becomes yellow, in consequence probably of the abstraction of water, for much heat is evolved, and the addition of water instantly restores the blue tint. Nothing is given off or absorbed, nor is carbon precipitated. When the sulphuric solution is neutralized by potassa, an intensely-blue precipitate falls, soluble in water, but insoluble in saturated solutions of the salts of potassa; it was, therefore, purified by alternate washing with solution of acetate of potassa and alcohol. When dry it acquires a copper colour, is very hygrometric, soluble in 140° of cold, and in a smaller proportion of hot, water. The cold solution, even when largely diluted, furnishes insoluble precipitates with salts of potassa, soda, lime, baryta, strontia, lead, and mercury. This substance has been called *Cerulein*, and exists in the precipitate as a *ceruleo-sulphate of potassa*: it appears to be a hydrate of indigo, in which 1 proportional of indigo is combined with 4 of water.

By limiting the action of the acid upon the indigo to three or four hours, (or at 100° to 20 minutes,) different results are obtained. One part of purified indigo was shaken in a phial with 10 of sulphuric acid till it became green: it was then poured into water, and filtered. The first washings of the substance upon the filter are to be rejected; but when the liquid passes of a blue colour, solution of chloride of potassium may be added, which throws down a *purple* precipitate, called by Mr. Crum, *Phenicin* (from *φοινίξ*). This substance is soluble in water and alcohol; it is converted by sulphuric acid into cerulin; it is precipitated by almost all saline substances of a purple colour; it appears to contain 1 proportional of indigo and 2 of water.

INDIGOGENE.—The extraordinary change which indigo, or rather its colouring principle, undergoes by the action of deoxidizing agents, has been studied by Liebig. (*Ann. de Ch. et Ph.*, xxxv.) He obtained *white* or *deoxidized* indigo (*indigogene*), as follows: $1\frac{1}{2}$ part of pure indigo, 2 parts

of protosulphate of iron, $2\frac{1}{2}$ parts of hydrate of lime, and from 50 to 60 parts of water, were digested together for 24 hours in a close vessel, which had previously been filled with hydrogen. The clear liquor over the sulphate of lime and oxide of iron had a yellowish-red colour, and was separated by a siphon filled with hydrogen, and mixed with diluted hydrochloric acid, containing some sulphite of ammonia dissolved; a dense white precipitate was formed, becoming blue in the air. This was gathered in a filter out of contact of air, and washed with boiled water containing sulphite of ammonia in solution, and dried at 212° , in close vessels, through which a current of hydrogen was continually passed. The upper surface of the mass became of a blue colour, but the lower remained of a dull white. This *white* substance was called *Indigogene*. It did not change colour in dry air, but under water became of a deep blue, which, by drying, assumed a coppery appearance. The blue substance volatilized by heat, without leaving any residue, forming purple vapours, which condensed, when cold, into crystals differing in nothing from sublimed indigo. Indigogene dissolves in alkalis without neutralizing them: it is also soluble in alcohol, but insoluble in water or acids.

A given quantity of this indigogene was acted upon by ammonia, and the weight of the undissolved blue portion ascertained; it appeared that the weight of the pure portion dissolved was 0.404 grammes (6.224 grains). The solution was put into an inverted jar, over mercury, and oxygen gas gradually passed in until absorption ceased, and then the liquid containing the precipitated indigo was evaporated to dryness at 212° . The weight of the substance was increased 11.5 per cent.

Not having obtained indigogene *perfectly* pure, M. Liebig did not attempt to analyze it for the ultimate composition. He remarks, that indigo is perhaps the only organic body from which one of its constituent parts may be taken without total decomposition; and which, by oxidation, passes to the state of a body having much analogy with peroxides.

Wöhler obtained deoxidized indigo by digesting indigo with sugar and excess of caustic potassa or soda: the sugar yields in this case formic acid.

L. Gmelin, in his *Handbuch*, gives the following as the probable composition of white deoxidized indigo, or indigogene:—

Nitrogen	1	14	12.07
Carbon	15	90	77.59
Hydrogen	4	4	3.45
Oxygen	1	8	6.89
Deoxidized indigo	1	116	100.00

and if *indigo-blue* be regarded as a *protoxide of indigogene*, the following view may be taken of its composition:—

					Crum.	De Royer and Dumas.	Ure.
Nitrogen .	1	14	11.29	11.26	13.74	10.00	
Carbon .	15	90	72.58	73.22	73.30	71.37	
Hydrogen .	4	4	3.23	2.92	2.80	4.38	
Oxygen .	2	16	12.90	12.60	10.16	14.25	
Indigo-blue	1	124	100.00	100.00	100.00	100.00	

and regarding *phenicin* as a *bihydrate*, and *cerulin* as a *quadrihydrate* of *indigo**, they will be constituted as follows:—

Nitrogen	1	14	9.86	9.91	} Indigo blue 1	. 124	. 87.33	
Carbon	15	90	63.38	64.62				
Hydrogen	6	6	4.22	3.98				
Oxygen	4	32	22.54	21.49				
Phenicin	1	142	100.00	100.00	or	1	142	100.00

Nitrogen	1	14	8.75	8.79	} Indigo blue 1	. 124	. 77.5	
Carbon	15	90	56.25	57.18				
Hydrogen	8	8	5.00	4.71				
Oxygen	6	48	30.00	29.32				
Cerulin	1	160	100.00	100.00		1	160	100.0

ACTION OF NITRIC ACID ON INDIGO.—The action of nitric acid on indigo was first examined by Mr. Hatchett. (*Additional Experiments on Artificial Tannin*, *Phil. Trans.*, 1805.) He found that this acid, diluted with about 2 parts of water, produced much effervescence when poured on powdered indigo, and gradually dissolved it; the solution, evaporated to dryness, left a yellowish residue, soluble in water, of an intensely-bitter taste, and composed partly of artificial tannin, and partly of a peculiar *bitter principle* combined with ammonia.

CARBAZOTIC ACID.—The action of nitric acid on indigo has subsequently been studied by Liebig, who finds a peculiar acid among the results afforded by treating indigo with excess of nitric acid, which he terms *Carbazotic acid*, and respecting the production and properties of which he has given the following details:—

A portion of the best indigo is to be broken into small fragments, and gently heated with eight or ten times its weight of nitric acid, of moderate strength. It will dissolve, evolving an abundance of nitrous vapours, and swelling up in the vessel. After the scum has fallen, the liquid is to be boiled, and nitric acid added as long as any disengagement of red vapours is occasioned by it. When the liquid has become cold, a large quantity of semi-transparent yellow crystals will be formed, and if the operation has been well conducted, no artificial tannin or resin will be obtained. The crystals are to be washed with cold water, and then boiled in water sufficient to dissolve them. If any oily drops of tannin form on the surface of the solution, they must be carefully removed by touching them with filtering-paper. Then filtering the fluid, and allowing it to cool, yellow brilliant crystalline plates will be obtained, which will not lose their lustre by washing. To obtain the substance perfectly pure, the crystals must be redissolved in boiling water, and neutralized by carbonate of potassa. Upon cooling, a salt of potassa will crystallize, which should be purified by repeated crystallizations. On mixing the first mother liquor with water, a considerable brown precipitate will be obtained, which being dissolved in boiling water, and neutralized by

* According to Berzelius, the action of sulphuric acid upon indigo is attended by the production of *indigo purple*, *sulphate of indigo*, and *hyposulphate of indigo*.

carbonate of potassa, will also furnish a quantity of the salt. All the potassa salt obtained in these operations is to be redissolved in boiling water, and nitric, hydrochloric, or sulphuric acid added; as the solution cools, the peculiar substance will be observed to form very brilliant plates of a clear yellow colour, generally in equilateral triangular forms. Sometimes crystals are not formed after the action of the nitric acid on the indigo, in which case the liquor must be evaporated, and water added, when the substance will precipitate, and must be purified as already described. Four parts of indigo yield one of the pure substance.

When the substance is heated, it fuses, and is volatilized without decomposition; when subjected to a sudden strong heat, it inflames without explosion, its vapours burning with a yellow flame, and a carbonaceous residue remaining. It is but little soluble in cold water, but much more in boiling water; the solution has a bright-yellow colour, reddens litmus, has an extremely bitter taste, and acts like a strong acid on metallic oxides, dissolving them, and forming peculiar crystallizable salts. Ether and alcohol dissolve the substance readily. When fused in chlorine or with iodine, it is not decomposed, nor does solution of chlorine affect it. Cold sulphuric acid has no action on it; when hot it dissolves it, but water separates it again without alteration. Boiling hydrochloric acid does not affect it, and nitro-hydrochloric acid only with great difficulty. These results show that no nitric acid is present in the substance, and other experiments prove that no oxide of nitrogen exists in it; it contains no oxalic or other organic acid, for when its salt is boiled with chloride of gold, the latter is not reduced. When heated to redness with oxide of copper, it gave a mixture of nitrogen and carbonic acid, in the exact proportion of 1 volume of the former to 5 of the latter. This was a constant result, and in no case was any sulphuric or other acid left in the copper. This compound, therefore, called *carbazotic acid*, is represented by Liebig as destitute of hydrogen, and as consisting of

Liebig. Mean of 4 expts.					
Nitrogen	3	42	16.67	16.2	
Carbon	15	90	35.71	35.0	
Oxygen	15	120	47.62	48.8	
Carbazotic acid	1	252	100.00	100.0	

THE CARBAZOTATES are crystallizable, bitter, and deflagrate or explode when heated. They detonate much more powerfully when heated in close vessels, than when heated in the air; and it is curious to observe, that those with bases yielding oxygen most readily, are those which explode with least force. By heating some of the salts previously mixed with chloride of potassium, &c., to retard the action, it appeared that no carbonic oxide, but only carbonic acid and nitrogen, were evolved during their decomposition by heat.

CARBAZOTATE OF AMMONIA forms very long, flattened, brilliant, yellow crystals, very soluble in water. Heated carefully in a glass tube, it fuses, and is volatilized without decomposition; heated suddenly, it inflames without explosion, and leaves much carbonaceous residue.

CARBAZOTATE OF POTASSA crystallizes in long yellow quadrilateral needles, semi-transparent and very brilliant; it dissolves in 260 parts of water at 60° Fahr., and in much less boiling water: a saturated boiling solution becomes a yellow crystalline mass, from which scarcely any fluid will run. Strong acids decompose it; yet when an alcoholic solution of carbazotic acid is added to a solution of nitre, crystallized carbazotate of potassa, after some time, precipitates. Alcohol does not dissolve it. When a little is gradually heated in a glass tube, it first fuses, and then suddenly explodes, breaking the tube to atoms; traces of charcoal are observed on the fragments. This salt precipitates a solution of the protonitrate of mercury, but not salts containing the peroxide, or those of copper, lead, cobalt, iron, lime, baryta, strontia, or magnesia. The slight solubility of this salt supplies an easy method of testing and separating potassa in a fluid. Even the potassa in tincture of litmus may be discovered by it; for, on adding a few drops of carbazotic acid, dissolved in alcohol, to infusion of litmus, crystals of the salt gradually separated. The saturated solution of the salt at 50° Fahr. is not troubled by chloride of platinum. The salt contains no water of crystallization. It was analyzed by converting a portion of it into chloride of potassium by hydrochloric acid. Its composition is,

				Liebig.
Potassa	1	48	16	16.21
Carbazotic acid . . .	1	252	84	83.79
Carbazotate of potassa	1	300	100	100.00

CARBAZOTATE OF SODA crystallizes in fine silky yellow needles, having the general properties of the salt of potassa, but soluble in from 20 to 24 parts of water, at 59°.

CARBAZOTATE OF LIME, obtained like the salt of baryta, forms flattened quadrangular prisms, very soluble in water, and detonating like the salt of potassa.

CARBAZOTATE OF BARYTA is obtained by heating carbonate of baryta and carbazotic acid with water. It crystallizes in quadrangular prisms of a deep colour, and dissolves easily in water. When heated, it fuses, and is decomposed with very powerful explosion, producing a vivid yellow flame: the explosion is as powerful as that of fulminating silver. A solution of chloride of potassium, to which carbazotate of baryta has been added, produces a precipitate of the potash-salt, and not more than 1½ per cent. of potash remains in solution. Carbazotate of baryta contains

				Liebig.				Liebig.
Baryta	1	77	23.5	23.4	1	77	20.59	20.87
Carbazotic acid	1	252	76.5	76.6	1	252	67.38	66.63
Water					5	45	12.03	12.50
Dry	1	329	100.0	100.0	Cryst. 1	374	100.00	100.00

CARBAZOTATE OF MAGNESIA forms very long indistinct needles, of a clear yellow colour; is very soluble, and detonates violently.

PROTO-CARBAZOTATE OF MERCURY is obtained in small yellow triangular crystals, by mixing boiling solutions of the carbazotate of potassa

or soda, and protonitrate of mercury. It requires more than 1200 parts of water for its solution: for its perfect purification, it should be heated with a solution of chloride of potassium, the insoluble portion separated whilst the liquid is hot, and the peculiar salt allowed to deposit as the temperature falls. When heated, it behaves like the salt of silver. It consists of

Protoxide of mercury	1	210	45.45	Liebig. 45.09
Carbazotic acid	1	252	54.55	54.91
Carbazotate of mercury	1	462	100.00	100.00

CARBAZOTATE OF LEAD may be formed by decomposing a salt of lead by carbazotate of potassa or soda; it is a yellow powder, but slightly soluble, and detonating by heat.

CARBAZOTATE OF COPPER is prepared by decomposing sulphate of copper by carbazotate of baryta; it crystallizes with difficulty, the crystals being of a fine green colour; it is deliquescent; when heated, it is decomposed without explosion, and even without inflammation.

CARBAZOTATE OF SILVER.—Carbazotic acid readily dissolves oxide of silver, when heated with it and water; and the solution, gradually evaporated, yields starry groups of fine acicular crystals of the colour and lustre of gold; the salt dissolves readily in water; when heated to a certain degree, it does not detonate, but flashes like gunpowder.

INDIGOTIC ACID.—By the action of *dilute* nitric acid on indigo, a peculiar acid, which appears perfectly distinct from the above, was obtained by Chevreul, and has been examined more in detail by Dr. Buff. It has been termed *Indigotic acid*.

To obtain it, nitric acid, of spec. grav. 1.285, was diluted with rather more than its weight of water, heated in a retort, and small portions of indigo in fine powder added as long as sensible effervescence was produced: a little water was added from time to time, to prevent the formation of carbazotic acid. The yellow liquid was separated, whilst hot, from the resinous matter, and by cooling deposited crystals of this acid of indigo. These were boiled with oxide of lead, filtered, and the salt produced decomposed by sulphuric acid whilst hot; on cooling, the liquor deposited the acid of indigo in yellowish-white crystals; these were separated, dissolved in hot water, neutralized by carbonate of baryta, the solution concentrated, and allowed to cool; yellow acicular crystals of a barytic salt were obtained, which, being washed with cold water, dissolved in hot water, and decomposed by acids, gave acicular crystals of this acid of indigo, white as snow; they were collected, and washed upon a filter, and shrank into a small space when dry, losing almost entirely their crystalline aspect.

Indigotic acid is white, having the lustre of silk; it has a weak, acid, bitter taste, reddens litmus, dissolves in any quantity in boiling water or alcohol, forming colourless solutions, but requires 1000 parts of cold water for its solution. It is volatile, and, being heated in a tube, fuses and sublimes without decomposition. When the fused acid is cooled, it crystallizes in six-sided plates. In the air it burns with a bright flame,

evolving much smoke. Nitric acid changes it into carbazotic acid. Neither chlorine, nor solution of chlorine, has any effect upon it. It gives a blood-red colour to solutions of the persalts of iron.

When decomposed by heat and oxide of copper, it yields nitrogen and carbonic acid; the proportions of these gases in volume being 1 and 15. These are exactly the same proportions which, according to Mr. Crum and Dr. Buff, are given by pure indigo itself; so that the nitrogen and carbon are probably in the same relation both in indigo and the acid of indigo. Dumas also states that the *indigotic acid* may be regarded as an oxide of indigo, but different authorities differ as to its equivalent. According to Buff, the neutral *indigotate of lead* consists of 37·38 oxide of lead + 62·62 indigotic acid, and accordingly the equivalent 180 may be assumed as that of indigotic acid, and it may be regarded as containing

				Buff.	Dumas.
Nitrogen	1	14	7·78	7·588	7·73
Carbon	15	90	50·00	49·575	48·23
Hydrogen	4	4	2·22		2·76
Oxygen	9	72	40·00	42·837	41·28
Indigotic acid	1	180	100·00	100·000	100·00

INDIGOTATE OF AMMONIA forms yellow, transparent, acicular prisms, much resembling the carbazotate of potassa, partly volatile without decomposition, and easily soluble in water.

INDIGOTATE OF POTASSA.—Orange-coloured, silky, opaque, clustered needles, anhydrous, and very soluble.

INDIGOTATE OF SODA.—Yellow, and very soluble.

INDIGOTATE OF BARYTA.—When carbonate of baryta is boiled in a solution of indigotic acid, and filtered, a yellow bitter solution is obtained, which yields yellow anhydrous fibrous crystals, composed of ($B + 13 \text{ ind}$). Ammonia added to this solution throws down a yellow powder, consisting of ($5 B + 3 \text{ ind}$).

INDIGOTATE OF LIME, OF STRONTIA, AND OF MAGNESIA, are yellow and soluble salts.

INDIGOTATE OF LEAD is thrown down in the form of a bulky pale-yellow precipitate, when a solution of indigotate of potassa is gradually added to excess of a hot solution of nitrate of lead. When washed with cold water, and dried at 212° , it forms a pale-yellow crystalline mass, rather more soluble in cold water than indigotic acid, and easily soluble in hot water. When digested in ammonia it becomes a yellow insoluble subsalt. These indigotates of lead consist of

				Buff.			Buff
Oxide of lead	1	112	38·4	37·38	2	224	55·4
Indigotic acid	1	180	61·6	62·62	1	180	44·6
Neutral	1	292	100·0	100·00	Subsalt 1	404	100·0
							100·00

INDIGOTATE OF IRON.—Indigotic acid dissolves hydrated peroxide of iron, and forms a salt which may be obtained in dark-red, or nearly black crystals, slowly soluble in cold water. The solution is dark-red.

INDIGOTATE OF COPPER.—Oxide of copper is soluble in indigotic acid. The salt separates from its solution in boiling water, in the form of a green flocculent precipitate.

INDIGOTATE OF MERCURY.—Indigotate of potassa produces a pale-yellow precipitate in protonitrate of mercury, which is insoluble in cold, and sparingly soluble in boiling water. From Buff's analysis it appears to be a sesquisalt = $(\text{Hg} + 1\frac{1}{2} \text{ ind})$.

INDIGOTATE OF SILVER.—Solution of indigotic acid readily dissolves oxide of silver: the solution blackens when long boiled. (CHEVREUL.) Neither indigotic acid, nor indigotate of potassa, produce any precipitate in nitrate of silver. Indigotate of silver forms pale-red acicular crystals, difficultly soluble in cold water. (BUFF.)

§ XI. FIXED OR FAT OILS. WAX.

THE proximate principles that we are now about to examine, are those in which hydrogen predominates, and which are characterized by the readiness with which they burn with flame: they are ternary compounds of carbon, hydrogen, and oxygen, and are applicable to numerous useful purposes.

FIXED OILS are generally obtained by pressure from certain seeds, such as the almond, linseed, and many others, and from the olive. The specific gravity of the fixed oils is below that of water, varying from 0.918 to 0.936. They are viscid or unctuous, and mostly insipid, or nearly so; they generally congeal at a temperature not so low as that required to freeze water, though a few remain liquid at very low temperatures. This is the case with linseed oil. A few of them are solid at the ordinary temperatures, and have been called *vegetable butters*. They are insoluble in water, but by the aid of mucilage may be diffused through it, forming *emulsions*.

If oil, which has been congealed by cold, be submitted to pressure between folds of bibulous paper, a dry, concrete, fatty matter is obtained, which Chevreul has called *Stearine**, (from $\sigma\tau\epsilon\alpha\rho$, tallow,) the paper absorbs a fluid matter, which does not congeal at a much lower temperature, and which, though it does not become rancid, acquires viscosity by exposure to air. This fluid part he has called *Elaine* or *Olein*, (from $\epsilon\lambda\alpha\iota\omicron\nu$, oil.) The relative proportions of these principles differ in the different oils. (*Ann. de Ch.*, tom. xciii. xciv.) See *Animal Oils*.

The greater number of the fixed oils undergo little other change by exposure to air than that of becoming somewhat more viscid, and acquiring a degree of rancidity. In this state they contain free acid, and redden vegetable blues. Some few, such as linseed and nut oil, and the oils of the poppy and hempseed, become covered with a pellicle, and, when thinly spread upon a surface, instead of remaining greasy, become hard and resinous; these are termed *drying oils*, and their drying quality is much improved by boiling them upon a small quantity of litharge.

The quantity of oxygen absorbed by some of the oils is very considerable.

* According to Lecanu (*Ann. de Ch. et Ph.*, LV. 192), the stearine of vegetable oils differs from that of animal fats, and is analogous to *margarine*.

Saussure exposed nut oil, for eight months, to oxygen gas; at first the absorption was trifling, but in the course of ten days it had taken up 60 times its volume, and in three months 145 times its volume, the absorption being most rapid in warm weather. It is well known that cotton and hemp, soiled with certain oils, are liable to spontaneous ignition; and Berzelius plausibly refers the phenomenon to the heat excited by the absorption of oxygen. No water was produced in Saussure's experiments, but carbonic acid was evolved, and the oil lost its greasy character and assumed a gelatinous appearance. (See some observations on the spontaneous combustion of cotton goods, by Dr. M. HALL, *Quarterly Journal*, 1st series, v. 367.)

These oils cannot be volatilized without decomposition, which takes place at a temperature of about 600° , and water is copiously formed, attended by the separation of carbonaceous matter, which causes the oil to blacken and grow thick; a portion of acetic acid is also at the same time formed. If the vapour be collected, it is found acrid, sour, and empyreumatic; it was formerly employed in pharmacy, under the name of *philosopher's oil*; and as it was often obtained by steeping a brick in oil, and submitting it to distillation, it was also called *oil of bricks*. Passed through a red hot tube, the fixed oils furnish a very large proportion of carburetted hydrogen gas; and when burned in the wicks of lamps they suffer a similar decomposition, and water and carbonic acid are the products of their combustion. The results of the distillation of the fixed oils have been examined by Dupuy, and by Bussy and Lecanu. The former subjected olive oil to its boiling point in a distillatory apparatus; white vapours passed over, which condensed into a liquid that became concrete on cooling; a fluid empyreumatic oil was also formed; and there remained a scanty portion of charcoal in the retort. The concrete portion was a mixture of oleic and margaric acids with a peculiar acrid, volatile principle; sebatic acid, and another acid matter, were also formed.

Bussy and Lecanu (*Ann. de Ch. et Ph.*, xxxi., xxxiii., and xxxiv.) distilled poppy oil at a temperature a little below 400° ; it exhaled an acrid odour, and yielded about one-third its weight of an oil which concreted on cooling, (a mixture chiefly of margaric, oleic, and benzoic acids.) This was succeeded by a liquid oil, which became turbid on exposure to air, was little soluble in alcohol, and not acted upon by the alkalis. Lastly, when the retort became red hot, a solid of the colour of realgar sublimed, which was without smell or taste, fusible in boiling water, and soluble in boiling alcohol and cold ether. Carburetted hydrogen, carbonic oxide, and carbonic acid, were also produced.

Chlorine effects a singular change in some of the fixed oils, converting them into a substance resembling hard tallow or wax. This is especially the case with castor oil. Hydrochloric acid is at the same time formed. Sulphur and phosphorus are soluble in the fixed oils; and with the former, linseed oil forms a brown fetid solution, known in Pharmacy as *balsam of sulphur*.

The stronger acids modify and decompose the fixed oils, and various products are the result, especially the stearic, margaric, and oleic acids, to which we shall afterwards advert. When olive oil is carefully mixed

with sulphuric acid, so as to avoid the heating of the mixture, a thick brown compound is formed, from which water separates the oil in an altered state, and retains in solution a peculiar compound (of hyposulphuric acid and organic matter?), which Chevreul has termed *sulpho-adipic acid*. When heat is applied to the mixture of sulphuric acid and oil, it blackens, sulphurous acid is evolved, and a coaly residue containing artificial tannin remains. (HATCHETT.) Concentrated nitric acid produces very complicated changes upon these oils, and sometimes the mutual action is so energetic, that the mixture inflames; by long boiling with dilute nitric acid, malic and oxalic acids are ultimately, but slowly, produced. The slow action of nitrous acid (hyponitrous?) upon several oils has been studied by Pelouze and Boudet. (*Ann. de Ch. et Ph.*, Lxix. 43.)

The fixed alkalis exert a remarkable action upon these oils, which terminates in the formation of *soap*, and a similar change is effected, though more slowly, by ammonia; these combinations we shall presently revert to. There are many other metallic oxides which appear to act more or less upon the oils in the manner of the alkalis. Sulphuret of carbon, some of the hydrocarbons, and a few of the metallic chlorides also dissolve in the fixed oils; there are, however, but few of the salts which are soluble in them to any extent.

The ultimate composition of the fixed oils has been accurately ascertained, but there are two difficulties in the way of determining their equivalents; the one is, that their absolute purity is difficultly ensured, and the other, that they do not combine with bases without undergoing change. The following are a few of the results of these analyses:—

	Olive Oil. Gay Lussac and Thenard.	Linseed Oil. Saussure.	Castor Oil. Ure.	Stearin of Olive Oil. Saussure.	Elain of Olive Oil. Saussure.
Carbon . .	77·213 . .	76·014 . .	74·00 . .	82·17 . .	76·03 . .
Hydrogen . .	13·360 . .	11·351 . .	10·29 . .	11·23 . .	11·54 . .
Oxygen . .	9·427 . .	12·635 . .	15·71 . .	6·30 . .	12·07 . .
	100·000	100·000	100·00	99·70	99·64

Saussure ascribes the loss in his analyses to nitrogen: he infers also, from the comparative analysis of stearin and elain, and from other results which I shall afterwards quote, that those oils which are most easily solidified, are those which contain the least oxygen, and that they are also the least soluble in alcohol.

The fixed oils are extremely numerous, and many of them have been examined and described: the following are a few details respecting their principal varieties, abridged chiefly from L. Gmelin and Berzelius.

1. DRYING OILS.—LINSEED OIL is expressed from the seeds of common flax (*Linum usitatissimum*). Cold-drawn, it is greenish-yellow and more viscid than when hot-drawn. Its specific gravity varies between 0·928 and 0·932. It dissolves in 5 parts of boiling alcohol, 40 of cold, and 1·6 of ether. A preparation of linseed oil, called *drying oil* or *painters' varnish*, is made by mixing a quart of the oil with about half an ounce of powdered litharge, and a quarter of an ounce of white vitriol, in a glazed pipkin, and heating it over a very gentle fire for four or five hours; the lower the heat, and the longer it is continued, the better

is the varnish. In this process the greater part of the oxide of lead is reduced. This, and other drying oils, and especially *nut oil*, form the basis of *printers' ink*, the history of which will be found in LEWIS'S *Phil. Commerce of the Arts*. The oil is heated and set fire to, and, after having been suffered to burn for half an hour, is extinguished, and boiled till it acquires a due consistency; in this state it is called *Varnish*, and is viscid, tenacious, and easily miscible with fresh oil, or with oil of turpentine, by which it is properly thinned, and afterwards mixed with about one-eighth part of lamp-black.

For white paint and light colours, unboiled linseed oil is used: it dries slowly, but does not injure the colour. There is a mixture of drying oil and mastic varnish, known to artists by the term *magilp*, of a gelatinous consistence, and an excellent vehicle for colours.

WALNUT OIL, expressed from the seeds of the walnut tree, (*Juglans regia*), has a specific gravity of about $\cdot 920$ at 60° ; it is inodorous, and as it dries better than linseed oil, is sometimes preferred by painters.

HEMP OIL, from hempseed, (*Cannabis sativa*), has an unpleasant odour, dissolves in all proportions of boiling absolute alcohol, but requires 30 parts of cold alcohol. It is much used in some parts of the north of Europe to burn, and for paints.

POPPY OIL, expressed from poppy-seed, (*Papaver somniferum*), is bland and insipid. Its specific gravity = $\cdot 924$. It dissolves in 25 of cold and 6 of boiling alcohol, and is used in some parts of Germany and France as a substitute for olive oil.

CASTOR OIL is the produce of the seeds of the *Ricinus communis*. It is pale yellow; its specific gravity at 55° is $\cdot 969$, at 75° = $\cdot 957$, at 212° = $\cdot 908$. (SAUSSURE.) It has a slightly nauseous odour and taste; it differs, however, much in these respects, and that which is at present used in medicine, and which is *cold-drawn* by pressure, is less acrid and purgative than the West India castor oil, formerly preferred for medical use, and which was often pressed with heat, or even boiled out of the seeds*. It congeals at about 0° . Exposed to air it gradually becomes rancid, thick, and at length congeals. It dissolves (in all proportions?) in absolute alcohol and in ether, by which foreign substances are occasionally separated from it. The products of the distillation of this oil have been examined by Bussy and Lecanu (*Journal de Pharm.*, xiii. 68); they obtained from them a peculiar acid, (*ricinic acid*), forming with magnesia and oxide of lead, salts soluble in alcohol, and resembling one of its products of saponification.

CROTON OIL.—This, which is the expressed oil of the seeds of the *Croton tiglium*, is used in medicine as a drastic purge. It has a brown or yellow colour, an acrid taste, and is operative in doses not exceeding a single drop; the oil, however, as met with in commerce, varies much in

* Guibourt ascribes the medicinal activity of castor oil to a peculiar volatile principle, which he says is expelled by heat, and considers the purgative power of the cold-drawn oil to exceed that of the oil obtained by aid of heat.

activity. When the seeds are digested in ether we obtain, according to Nimmo, 60 per cent. of their weight of oil, of which two-thirds are soluble in alcohol and purgative; one-third is bland and inert. The acrid principle of the croton-seed appears to be *acid*, and has been termed, by Pelletier and Caventou, *Iatrophic Acid*, from erroneously supposing the seeds to be the produce of the *Iatropa curcas*. Brandes has since examined the acid, and calls it *Crotonic Acid*.

2. GREASY OILS.—ALMOND OIL is expressed from sweet and bitter almonds; it is pale yellow, and becomes colourless when long exposed to light; it soon grows rancid, especially if in contact of oxygen. Its specific gravity at 60° is .91 to .92. When cooled down to 15° it yields 0.24 margarin, and 0.76 elain; the latter does not congeal at 0°. Almond oil is soluble in 25 parts of cold and 6 of boiling alcohol; it readily dissolves in ether.

OLIVE OIL is extracted from the fleshy part of the olive (the fruit of the *Olea Europæa*). It is pale yellow, and its specific gravity is about .910 at 60°. When cooled down to 0° and expressed, it yields about 0.28 margarin, and 0.72 elain: it often deposits margarin at common temperatures, a portion of which is generally found at the bottom of the jars and casks in which it is kept. The quality of this oil is very various: the best is obtained by gentle pressure without heat; that which is procured by the aid of heat, and of a greater degree of pressure, is called *second oil*; and a very inferior kind is ultimately extracted by boiling the expressed cakes in water. Fine olive oil is extremely bland and tasteless, or at least has only a slight nutty flavour: the commoner kinds, (that, for instance, called *Gallipoli oil*,) are disagreeable both in smell and taste. Olive oil is sometimes adulterated with the cheaper expressed oils, especially with rape and poppy oil.

If pernitrate of mercury, made by dissolving 6 parts of mercury in 7.5 parts of nitric acid of specific gravity 1.36, at common temperature, be mixed with olive oil, in the course of a few hours, the mixture, if kept cold, becomes solid; but if mixed with the oil of grains, it does not solidify. Poutet (*Ann. de Ch. et Ph.*, xii. 58) has, therefore, proposed this as a test of the purity of olive oil; for the resulting mixture, after standing twelve hours, is more or less solid, as the oil is more or less pure. The nature of the compound formed by olive oil and the nitrate of mercury, has been examined by M. F. Boudet (*Ann. de Ch. et Ph.*, i. 391). I shall afterwards revert to it.

Rousseau states that olive oil is the worst conductor of electricity of all the fat oils, and suggests a mode of applying this test to the detection of its adulterations.

Of all the oils, that of olives is least apt to become viscid and glutinous, and hence is preferred for greasing delicate machinery, as especially watch and clock-work. For this purpose the elain may perhaps be preferable to the entire oil. Watchmakers are in the habit of preparing the oil for this purpose, by keeping a piece of sheet-lead, or some shot in it, and exposing it in a corked bottle to light. A white matter is gradually deposited, and the oil ultimately becomes clear and colourless, and no longer affected by the metal: this subject has not been scientifically investigated.

BEECH-NUT OIL.—The decorticated nuts of the beech-tree (beech-mast) yield about 15 per cent. of oil resembling olive oil, and a larger quantity when aided by heat; the remaining cake is a better food for cattle than common oil-cake.

OIL OF BEN is procured by expression from the decorticated seeds of the *Guilandia moringa*, a tree which grows in Ceylon, Ethiopia, Egypt, and Arabia. The oil is perfectly inodorous, and does not readily grow rancid, hence its excellence for the preparation of certain *scented oils*, such as those of the jasmine, tuberose, &c.

RAPE OIL is expressed from the seeds of the *Brassica napus*, and *rapa*. Its specific gravity at 60° is .912. This, and some other of the fat oils, contains a principle in solution, which interferes with its combustibility, and which may be abstracted by agitating the oil with about 2 per cent. of sulphuric acid, and afterwards washing it with 2 or 3 parts of water, with which it is left for two or three weeks, at a temperature between 75° and 80°; it gradually forms a deposit, from which it is drawn off, and filtered, and is then fit for burning in lamps. *Colsa* or *cole-seed oil* is a better kind of rape oil, extracted from the *Brassica campestris*, var. *oleifera*.

MUSTARD-SEED OIL is expressed from the seed of the *Sinapis alba* and *nigra*; the bruised seed yields about one-fifth its weight of a mild, inodorous, thick, amber-coloured oil; specific gravity .915 at 60°, soluble in 1000 parts of alcohol (specific gravity .833), and in 4 of ether. Alcohol extracts from it a peculiar acid (the *sulphosinapic**), and a crystallizable fatty matter, which is not saponifiable.

3. CONCRETE OILS. VEGETABLE BUTTERS.—The principal oils of this class are the following.

COCOA-NUT OIL, pressed, or boiled, out of the nut of the *Theobroma cacao*. When washed it is white, of a peculiar odour, and of the consistence of tallow: its specific gravity = .910. It fuses at about 125°. Its

* *Sulphosinapic acid* was found by Henry and Garot (*Jour. de Chim. Med.* 1.) in mustard, radish, and turnip-seed, and in the root of the horse-radish. 3 parts of expressed mustard oil and 4 of strong alcohol were mixed and often shaken together. After 3 days the yellow alcohol was poured off, and two-thirds abstracted by distillation: on cooling, the residue deposited the fatty matter above-mentioned, and the remaining liquid was decanted off, and left to spontaneous evaporation: it now deposited a granular mass, which by continuous digestion in ether, yields to that solvent a red fat, and the remaining matter (insoluble in ether) was dissolved in water, and left to spontaneous evaporation: scattered crystals were thus obtained, of a yellow colour, bitter pungent taste, and sulphurous odour. The composition of these crystals of *Sulphosinapic acid* is remark-

able, as essentially including five elementary substances, namely,

Sulphur . . .	17.33
Carbon . . .	49.50
Hydrogen . . .	8.30
Oxygen . . .	11.91
Nitrogen . . .	12.96

100.00

Berzelius has thrown out the suggestion that this acid may be a compound of hyposulphurous acid, and an organic base. The *Sulphosinapates* of the alkaline bases are crystallizable, but the equivalent of the acid has not been satisfactorily determined. It yields precipitates in the solutions of acetate of lead, protonitrate of mercury, nitrate of silver, and sulphate of copper. But the accuracy of all these conclusions is rendered doubtful by Pelouze, (*Ann. de Ch. et Ph.*, xiv. 214.)

elain is used as a lamp oil, and its *stearin* or *margarin* for the manufacture of candles.

PALM OIL.—Many of the palms produce a hard nut, like the date-stone, but abounding in oil: of these the principal are the *Cocos butyracea* and *Elæis guineensis*. These oils are used for soap, candles, &c., and the *stearine* and *elain* employed as the preceding.

NUTMEG OIL is the expressed oil of the common nutmeg; it is yellow, and smells of the essential oil. It is largely prepared in Holland, and occasionally used in medicine. According to Schrader, 16 ounces of the concrete expressed oil of nutmeg contain 7 of hard concrete oil, $8\frac{1}{3}$ yellow butyraceous oil, and $\frac{2}{3}$ volatile oil. Cold alcohol dissolves the volatile and the soft oil, and leaves the harder oil. When nutmeg oil is boiled in 4 parts of alcohol, it is entirely dissolved, and the harder fatty portion is deposited as the solution cools. Marrow, or common fat, scented by a little oil and powder of nutmeg, and coloured by annatto, is sometimes substituted for this oil: the fraud is detected by the insolubility of this artificial mixture in 4 parts of boiling alcohol. (BOLLAERT, *Quarterly Journal*, xviii. 317.)

WAX.—This principle exists in many plants; it may be obtained by bruising and boiling them in water: the wax separates and concretes on cooling. The berries of the *Myrica cerifera*, and the leaves and stem of the *Ceroxylon*, afford considerable quantities of wax by this process. (BOSTOCK, NICHOLSON'S *Jour.*, vol. iv., BRANDE, *Phil. Trans.*, 1811.) The glossy varnish upon the upper surface of the leaves of many trees is of a similar nature; and though there are shades of difference, these varieties of wax possess the essential properties of that formed by the bee; indeed, it was formerly supposed that bees merely collected the wax already formed by the vegetable, but Huber's experiments show that the insect has the power of transmuting sugar into wax, and that it is in fact a secretion.

BEES'-WAX.—White wax, or bleached bees'-wax*, is colourless and insipid; its specific gravity is about .96: it is insoluble in water, and fusible at a temperature of about 150°; at a higher temperature it is converted into vapour, and may be distilled with little other change than the production of a small portion of stearic acid, and at a red heat it burns in the contact of air with a bright flame. It is sparingly soluble in boiling alcohol and ether, and is deposited as the solutions cool. 20 parts of boiling alcohol dissolve about 1 of bees'-wax, of which not more than one-fifth is retained at the temperature of 60°, and this is thrown down by the addition of water. Cold ether appears without action on wax, but boiling ether takes up about one-tenth of its weight, and deposits nearly the whole on cooling. The fixed oils, when assisted by heat, readily dissolve it, and form a compound of variable consistency, which is the basis of *cerates* and *ointments*. Some of the volatile oils also dissolve wax, when aided by heat. It combines with the fixed alkalis, forming imperfect soapy compounds of very difficult solubility, and from which the acids

* The bleaching of bees' wax is effected by exposing it in thin ribands upon the bleaching ground. It may be whitened by chlorine, but wax so bleached never burns well; it smells of, and appears to contain, chlorine.

separate the wax in an unaltered state. The acids, at common temperatures, scarcely act upon wax; hence the advantage of *wax-lute* for the retention of corrosive vapours. At the fusing-point of wax it combines with sulphuric acid, and the solution congeals on cooling. Hydrochloric acid has no action upon it; nitric acid, after long boiling, very slowly converts a portion of it into oxalic acid.

MYRICIN.—When myrtle wax is digested in boiling alcohol, it affords, according to Dr. John, a soluble and insoluble portion; he has called the former *cerin*, the latter *myricin*. Cerin is insoluble in water and in cold alcohol and ether, but dissolves in those liquids when heated. Myricin is insoluble, under all circumstances, in alcohol and ether.

CERINE.—This term has been applied by Chevreul to a principle resembling wax, which he separated from *cork*; it is less fusible than wax, more soluble in alcohol, and partly converted into oxalic acid by the action of nitric acid.

Bees'-wax has been analyzed by Gay Lussac and by Dr. Ure, with the following results:—

	Gay Lussac.	Ure.
Carbon .	81.874 . . .	80.60
Hydrogen .	12.672 . . .	11.47
Oxygen .	5.544 . . .	7.93
	100.000	100.00

According to Oppermann, pure vegetable-wax differs slightly from bees'-wax, in the ratio of its elements.

§ XII. SOAPS. SAPONIC, OR ADIPOSE ACIDS.

PROCESS OF SAPONIFICATION.—When the fat oils are digested with caustic alkali, a compound results, long and well known under the name of *soap*; with the real nature, however, of this compound we were not acquainted, till the subject was investigated by Chevreul, who, in the masterly researches already quoted (see also *Recherches Chimiques sur les Corps gras*, Paris, 1823), demonstrated the nature of the changes which the oils undergo, and discovered a number of new acid substances into which they are converted. These experiments have principally reference to *animal oils*, and the general account of them ought strictly to be referred to the chemical history of animal products: but the *vegetable* oils and fats are in many of their properties identified with, and in all so closely analogous to the corresponding products of animals, that I shall give an abstract of the whole subject in this place.

The various kinds of *soaps* differ chiefly in the oil or fat used in their manufacture, for the alkali which is employed is, for *hard soaps*, almost invariably soda: by the mutual action of the oil and alkali the stearic and elaic components of the former are converted into one or more *acids*, which combine with the soda, so that in this respect, soaps may be correctly spoken of as a class of *salts*, deriving their peculiarities almost exclusively from the *acids* which they contain. The soap of olive oil and soda may be taken as a specimen of this article: it is made as follows:—5 parts of barilla, or an equivalent proportion of other carbon-

ate of soda, are mixed with 1 of lime, and a proper quantity of water. In this way a *ley*, or solution of *caustic soda*, is obtained, which is boiled in an iron pot with *six parts* of the oil, till the *soap* separates: this separation of the soap from the water, is accelerated by the addition of common salt; it is then suffered more perfectly to congeal, and in a few days becomes hard enough to cut into forms. (AIKIN'S *Dictionary*—Art. SOAP.) The best soaps are made with olive oil and soda; in this country *animal fat* is usually employed for the common soaps, to which resin and other substances are occasionally added. *Soft Soap* is made with potassa and some of the common oils; even fish oil is often used, and hence peculiar compounds or *salts* result, as we shall presently find*.

The general properties of soap are the following. It furnishes a milky solution with water. It dissolves in alcohol, and the solution, if concentrated, is of a gelatinous consistency, and by carefully distilling off the alcohol, a *transparent soap* is obtained. The acids, and the greater number of salts, decompose soap, forming, in most cases, a compound of difficult solubility; hence, *hard waters* are unfit for washing, in consequence of containing sulphate of lime; hence, also, the *alcoholic solution of soap* is useful as a test for ascertaining the fitness of water for this purpose, which, if it becomes very turbid, cannot in general be used for washing.

When the above soap is decomposed by dilute sulphuric acid, sulphate of soda is formed, but the oil is not separated in its former state, but has acquired the new properties we are about to notice: there is also formed during the mutual action of the oil and alkali, a compound discovered by Scheele, and called by him the *sweet principle*: it has since been termed *glycerine* (from $\gamma\lambda\upsilon\kappa\upsilon\varsigma$, *sweet*).

GLYCERINE may be obtained by saturating the alkaline mother-liquor, from which the soap has concentered, by dilute sulphuric acid, adding a little carbonate of baryta to remove any slight excess of the acid, filtering, and evaporating to the consistency of thin syrup, to which alcohol is then added, which dissolves the *glycerine* and leaves the alkaline sulphate. Glycerine is not crystallizable; it has a pure sweet flavour, and cannot be deprived of water without decomposition. When distilled, a portion passes over unaltered. Heated in the air it burns with a blue flame. It is very difficult of conversion into oxalic acid by the action of nitric acid, and has very little tendency to fermentation.

When glycerine is obtained by evaporating its alcoholic solution in vacuo, it is in the state of *hydrate*. Dumas represents its ultimate components as follows†:—

					Dumas.
Carbon	3	:	18	:	48·7
Hydrogen	3	:	3	:	8·1
Oxygen	2	:	16	:	43·2
Glycerine	1		37		100·0
					100·00

* The fixed oils also form peculiar compounds with, or are *saponified* by *hydrated oxide of lead*, when aided by heat, forming the substance usually termed *plaster*; with the oxides of mercury and

bismuth they produce very similar combinations.

† (See FREMY, *Ann. de Chim.*, lxxiii. 25; VOGEL, *Journal de Pharm.*, iv. 255; and CHEVREUL, *Recherches*.)

And, as containing in the state of *hydrate* 1 atom of water ($37+9=46$),
or

Anhydrous glycerine = $(3\text{ car} + 3\text{ h} + 2\text{ o})$.

Hydrated do. = $(3\text{ car} + 4\text{ h} + 3\text{ o})$.

Having thus stated the general results of saponification, I shall give an outline of the properties of the *acids* generated by the action of the alkalis, and of such other analogous bodies as are included by Dumas under the term *Adipose acids*. (*Acides gras*, see *Traité de Ch. app. aux Arts*, v. 239.)

ADIPOSE ACIDS. SAPONIC ACIDS.—These substances, when *solid*, resemble fat, wax, or spermaceti; when *liquid*, they look like thin oils. They are mostly fusible at temperatures below 212° ; they are more or less volatile, colourless when pure, lighter than water, soluble in alcohol and ether, and in the fixed and volatile oils. They contain much less oxygen than is requisite to convert their carbon and hydrogen into carbonic acid and water, and hence are eminently inflammable. They are little affected by air or by acids at common temperatures: heated with sulphuric or nitric acid they are decomposed: they redden litmus. Their equivalent is always a high number. Aided by heat they decompose the carbonates.

The greater number of these acids are not found in a separate state, but they appear to exist in oils and fats in union with an organic base. They are divided by Dumas into, 1. Those which are insoluble in water, and which only admit of distillation in *vacuo*: 2. Those which are soluble in water, and which may be distilled over with water in the ordinary way.

1. **STEARIC ACID.**—This acid is the most characteristic product of the saponification of suet, and other hard or not easily-fusible fats. It is obtained by decomposing *stearate of potassa*, by dilute hydrochloric acid. It melts at 158° and concretes into a mass of shining crystals. Boiling anhydrous alcohol dissolves it in all proportions, and the solution yields nacreous crystals: it is soluble in its weight of ether; it is volatile in *vacuo*: it burns in the air like wax. It is soluble in cold sulphuric acid, and decomposed by it when heated: it is not acted on by cold nitric acid, but the boiling acid dissolves and modifies it. This acid consists of*

				Chevreul.	
Carbon	35	210	79·85
Hydrogen	33	33	12·55
Oxygen	$2\frac{1}{2}$	20	7·60
Anhydrous stearic acid	1		263		100·00
					100·000

The *hydrated stearic acid* consists of 1 atom anhydrous acid and 1 water ($263+9=272$), or

Anhydrous stearic acid $(35\text{ car} + 33\text{ h} + 2\frac{1}{2}\text{ o})$.

Hydrated do. $(35\text{ car} + 34\text{ h} + 3\frac{1}{2}\text{ o})$.

Stearic acid has lately been advantageously employed as a substitute

* The atomic composition of stearic acid, as given by Dumas, is $(70\text{ car} + 66\text{ h} + 5\text{ o})$, which would produce the equivalent 526, or double that in the text.

for wax in the manufacture of candles: for this purpose tallow is saponified by lime; the soap of lime is decomposed by dilute sulphuric acid, and the resulting stearic and oleic acids are separated by pressure. The oleic acid is used in the manufacture of soap; the stearic acid, when thoroughly purified, is made into candles. (The process of manufacture is described by M. Golfier-Besseyre, *Ann. de Ch. et Ph.*, LXX. 154.)

STEARATE OF AMMONIA.—Stearic acid absorbs gaseous ammonia, and forms a white inodorous compound, of an alkaline taste. It dissolves in boiling water, and the solution deposits nacreous crystals of *bistearate*.

STEARATE OF POTASSA is formed by boiling 1 part of stearic acid and 1 of caustic potassa in 10 of water: it falls in white opaque grains, which may be purified by solution in 15 to 20 parts of boiling alcohol: it falls, as this solution cools, in brilliant scales. Stearate of potassa may also be obtained by treating the soap of potassa with alcohol. This soap is prepared by boiling 100 parts of mutton-suet and 25 of caustic potassa in 100 of water, agitating the mixture till a homogenous compound is obtained: it is a mixture of *stearate*, *oleate*, and *margarate of potassa*: the two last are abstracted and retained by warm alcohol, which deposits the stearate. It consists of

				Chevreul.
Potassa	1	48	15.4	15.29
Stearic acid	1	263	34.6	34.71
Stearate of potassa	1	311	100.0	100.00

BISTEARATE OF POTASSA.—1 part of the above soap is dissolved by heat in 6 of water, and then 50 or 60 parts of cold water are added to the solution: a nacreous substance is deposited, composed of bistearate and bimargarate of potassa: this is dissolved in 20 to 24 parts of boiling alcohol (specific gravity 0.82), and during cooling, crystals are deposited, which, when dissolved in alcohol a second time, and again crystallized, are *bistearate of potassa*. It forms soft silvery scales, infusible at 212°, insoluble in cold water, but resolved by boiling water into potassa and *quadristearate*. It is soluble in boiling alcohol, 100 parts of which take up 27 of bistearate of potassa, but only retain 0.36 at 75°. The crystallized bistearate of potassa consists of

				Chevreul.
Potassa	1	48	3.2	3.075
Stearic acid	2	526	90.3	90.075
Water	1	9	1.5	1.850
Crystallized bistearate of potassa	1	533	100.0	100.000

STEARATE OF SODA.—The action of soda on stearic acid resembles that of potassa; and a stearate and bistearate, corresponding in composition with the above, are produced, but they are less soluble than the salts of potassa.

STEARATE OF LIME is a white, fusible, tasteless powder, thrown down when a boiling solution of neutral stearate of potassa is added to a solution of chloride of calcium. It consists of

				Chevreul.
Lime	1	28	9.6	9.96
Stearic acid	1	263	90.4	90.04
Stearate of lime	1	291	100.0	100.00

STEARATE OF BARYTA is formed by mixing hot solution of stearate of potassa with nitrate of baryta: it is a white, fusible, insipid powder. It contains

Baryta	1	77	22.6	Chevreul.
Stearic acid	1	263	77.4	22.31
Stearate of baryta	1	340	100.0	77.69
				100.00

STEARATE OF LEAD is white, fusible, and insoluble in water: it is formed by the action of a boiling solution of stearate of potassa on nitrate of lead. It consists of

Oxide of lead	1	112	29.87	Chevreul.
Stearic acid	1	263	70.13	29.5
Stearate of lead	1	375	100.00	70.5
				100.0

STEARONE.—When stearic acid is distilled with a fourth-part of quicklime, a substance is obtained sparingly soluble in ether and alcohol, concrete at common temperatures, but fusible at about 180°. (Bussy, *Jour. de Phar.*, xix. 643.) It consists of

Carbon	68	408	85.3
Hydrogen	62	62	13.0
Oxygen	1	8	1.7
Stearone	1	478	100.0

STEARINE.—The origin of this term and the substance to which it is applied, derived from olive oil, have been already noticed. The purest form of *Stearine* is procured by digesting purified mutton suet in cold ether, as long as it dissolves any part of it: the residue, dried by pressure between folds of blotting paper, is of a crystalline texture, semitransparent, friable, and fusible at about 110°. It is not soluble in cold alcohol; hence, when dissolved in boiling alcohol, it is deposited on cooling. It is only very sparingly soluble in cold ether; more so in boiling ether. A hot and concentrated solution of caustic potassa dissolves and saponifies it, forming a compound soluble in cold alcohol, and in water: this solution, decomposed by diluted hydrochloric acid, yields a precipitate of pure stearic acid, and glycerine is found in the residuary mother-liquor. 100 parts of stearine yield 96.8 stearic acid and 8 glycerine. Stearine is a compound of

Carbon	73	438	Dumas.
Hydrogen	69	69	78.02
Oxygen	7	56	12.20
Stearine	1	563	9.78
			100.00

and these numbers are equivalent to 2 atoms of anhydrous *stearic acid* + 1 of anhydrous *glycerine*: or

$$\text{Stearic acid} = (70 \text{ car} + 66 \text{ h} + 5 \text{ o})$$

$$\text{Glycerine} = (3 \text{ car} + 3 \text{ h} + 2 \text{ o})$$

$$\text{Stearine} = (73 \text{ car} + 69 \text{ h} + 7 \text{ o})$$

So that upon this view stearine is a *bistearate of glycerine*; the glycerine being the organic base.

II. MARGARIC ACID, so named from its pearly lustre, (*μαργαριτη, a pearl*), bears a striking resemblance to stearic acid. It is obtained by decomposing the *margarate of potassa*, or *margarate of lead*, by hot and very dilute hydrochloric acid: it fuses at 140° , and in respect to fusibility and solubility, is intermediate between stearic and oleic acids. It is composed, in its *anhydrous* state, of

			Chevreul.	Berzelius.
Carbon	35	210	79.053	78.38
Hydrogen	33	33	12.010	12.59
Oxygen	3	24	8.937	9.03
Margaric acid	1	267	100.000	100.00

I have adopted the atomic composition suggested by Berzelius*, because it refers to the purest form of margaric acid, and represents it as an oxide of the same base (or hydrocarbon) as the stearic acid. This view was originally adopted by Chevreul, who then applied to it the name of *margarous acid*.

MARGARATE OF AMMONIA is formed as the corresponding *stearate*.

MARGARATE OF POTASSA.—This salt may be obtained from the *soap of olive oil*, from which alcohol, very moderately heated (at 70 or 80°), abstracts the *oleate*, and leaves the *margarate of potassa*. (See *Margarine*.) Chevreul procured it from human, and from goose fat, saponified by potassa. It is softer, more fusible, and more soluble in alcohol than the *stearate of potassa*. It consists of

			Chevreul.
Potassa	1	48	15
Margaric acid	1	267	85
Margarate of potassa	1	315	100

BIMARGARATE OF POTASSA may be obtained as the *bistearate*; it crystallizes with 1 atom of water. Its hot aqueous solution, when decomposed by dilute hydrochloric acid, yields a precipitate of margaric acid.

MARGARATE OF SODA closely resembles the salt of potassa. The neutral margarate is soluble in 10 parts of water, at 175° .

MARGARATE OF LEAD.—With oxide of lead, the margaric acid forms a neutral, a basic, and an acid salt. A mixture of margarate and oleate of lead (as obtained by double decomposition, from a soap of olive oil) may be separated by cold ether, which leaves the margarate but dissolves the oleate.

MARGARONE.—A substance under this name is described by Bussy (*Jour. de Phar.*, xix. 635), among the products of the destructive distillation of a mixture of margaric acid with one-fourth its weight of lime. It is said somewhat to resemble *paraffine*, and to consist of ($68 \text{ car} + 67 \text{ h} + 2 \text{ o}$), numbers which are equivalent to hydrocarbon ($67 \text{ car} + 67 \text{ h}$) and carbonic acid ($\text{car} + 2 \text{ o}$). Its theoretical relations to paraffine and to margaric acid, are pointed out by Dumas.

* Chevreul gives ($70 \text{ car} + 65 \text{ h} + 6 \text{ o}$) = 533. Gmelin represents margaric acid by the equivalent 266, or ($35 \text{ car} + 32 \text{ h}$ + 30), or 64 instead of 65 atoms of hydrogen, if doubled.

MARGARINE.—This substance forms a part of mutton suet, hogs' lard, and some other animal fats: it appears to form the greater portion of the concrete part of olive oil, already mentioned, and when that substance is dried in bibulous paper, dissolved in ether, and left to spontaneous evaporation, the white flakes which are deposited are *margarine*. Margarine is distinguished from stearine by its greater fusibility. It is so far soluble in cold ether, that, at 65° , 2 parts are retained in permanent solution by 5 of ether. A solution of 2 parts of margarine in 10 of ether, is permanent at 60° , and does not begin to deposit till cooled down to 54° . The atomic constitution of margarine has not been accurately determined.

III. OLEIC ACID.—This acid is obtained by the decomposition of *oleate of lead*, or *oleate of potassa*, by a solution of tartaric acid: it separates in the form of an oil, and is to be washed with hot water: it often contains margaric acid, which it deposits by cautious cooling: when pure, it remains transparent at 32° . It resembles a colourless oil, of a slightly rancid taste and smell; its specific gravity is 0.898 at 65° . A few degrees below 32° , it concretes into a white acicularly-crystalline mass; it is not soluble in water, but is taken up in all proportions by alcohol of the specific gravity .822. It reddens litmus; mixes readily with stearic and margaric acids, and behaves like them when subjected to distillation. According to Chevreul, *anhydrous oleic acid* may be regarded as a compound of

					Chevreul.
Carbon . . .	35	210	81.08	80.942	
Hydrogen . . .	29	29	11.20	11.359	
Oxygen . . .	$2\frac{1}{2}$	20	7.72	7.699	
Oleic acid	1	259	100.00	100.000	

The *crystallized acid* includes 1 atom of water.

OLEATE OF AMMONIA.—Liquid ammonia rapidly dissolves oleic acid; heat is evolved, and a gelatinous mass, soluble in water, is formed.

OLEATE OF POTASSA.—This salt may be best extracted from the *soap of linseed oil*, which is dried, and digested in cold anhydrous alcohol; the clear solution is evaporated, and the residue again treated by cold anhydrous alcohol, by which any trace of margarate of potassa is left undissolved. The solution now contains pure *oleate of potassa*, and when slowly evaporated yields it, sometimes in an imperfectly-crystallized mass; its taste is alkaline and bitter: mixed with 2 parts of water it forms a transparent jelly: with 4 of water the solution is viscid; it absorbs moisture from the air. In the voltaic circuit it yields oleic acid at the positive, and potassa at the negative pole. At 122° alcohol dissolves its own weight of this salt, and the compound gelatinizes on cooling. Chevreul has also described a *binoleate*.

The *anhydrous oleate of potassa* consists of

				Chevreul.
Potassa . . .	1	48	15.19	
Oleic acid . . .	1	259	84.81	
Oleate of potassa	1	307	100.00	

OLEATE OF SODA is an easily-soluble salt.

OLEATE OF BARYTA is insipid, insoluble in water, very sparingly soluble in boiling alcohol, and soluble in oleic acid.

OLEATE OF COPPER is green, and easily fusible.

OLEATE OF LEAD is liquid at 77° , and viscid at lower temperatures: it is soluble in alcohol and ether.

OLEONE is a liquid product obtained by distilling oleic acid with lime.

ELAIDINE.—M. Poutet's test of the purity of olive oil has been above adverted to (p. 1132). The action of *nitrous acid* upon oil has been examined by M. Felix Boudet (*Ann. de Ch. et Ph.*, L. 391); he finds that when *olive* oil is shaken with a mixture of 3 per cent. of nitrous, and 9 of nitric acid, it solidifies in the course of an hour: that linseed oil, nut oil, poppy oil, hempseed oil, and beech-mast oil, are not so solidified: almond oil, and rape oil, are more slowly but similarly changed. *Castor oil* is also solidified, but the product is distinct*. M. Boudet applies the term *Elaidine* to the above product; and when saponified by potassa, it yields a peculiar fat acid, which he calls *Elaidic acid*†.

* Bussy and Lecanu (*Jour. de Phar.*, xiii.) have elaborately examined the products of castor oil, and have obtained from it, as results of saponification, *margaritic*, (not *margaric*), *ricinic*, and *elaiodic* (not the *elaïdic* acid of Boudet) acids. When castor oil is solidified by hyponitrous acid, (or by nitrate of mercury?) it yields a substance distinct from elaidine, called by Boudet *palmine*. When *palmine* is saponified, and the soap decomposed by an acid, *palmic acid* is separated.

† *Rocellic*, *valerianic*, and *esculic* acids, are placed by Dumas among the fat acids. *Rocellic acid* was discovered by Heeren, in the *Rocella tinctoria*: he obtained it by digesting the lichen in liquid ammonia, precipitating by chloride of calcium, and decomposing the *rocellate* of lime by hydrochloric acid, when *rocellic acid* subsides: it is washed, and purified by solution in ether, which afterwards deposits it in silky crystals, fusible at 265° : soluble in twice their weight of boiling alcohol, and composed, according to Liebig, of $(16\text{ car} + 16\text{ h} + 4\text{ o})$. The *rocellates* are analogous to soaps.

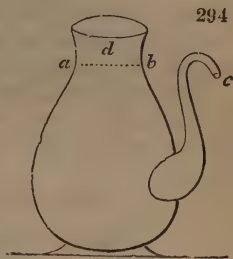
Valerianic or *valeric acid*, passes over with essential oil when the root of the *Valeriana officinalis* is distilled with water:

the product is mixed with carbonate of magnesia and water, and distilled: the oil passes over, and *valerianate of magnesia* remains: to this, dilute sulphuric acid is added, by which it is decomposed, and the *valerianic acid* may now be obtained by distillation, partly floating upon the water, and partly dissolved in it. It is a colourless oily liquid, smelling strong of valerian, specific gravity 0.94, acrid and acid to the taste, soluble in 30 parts of water, and in all proportions of alcohol. According to Essling, as quoted by Dumas, this acid in its oily form is a *hydrate*, composed of $(10\text{ car} + 10\text{ h} + 4\text{ o})$, the *anhydrous acid* being represented by the equivalent = $(10\text{ car} + 9\text{ h} + 3\text{ o})$.

Esculic acid was obtained by Fremy, by digesting pulverized horse-chestnuts in alcohol: the solution left, on evaporation, a peculiar yellow viscous matter, probably identical with the *saponin*, obtained by Bussy (*Jour. de Phar.*, xix.) from the root of the Egyptian *Saponaria*, (*Gypsophila struthium*?). This matter, when digested with solution of potassa, yields a soapy compound, from which the acids separate *esculic acid*. Such details respecting its nature and properties as have been ascertained, are given by Dumas (*Chim. app. aux Arts*, v. 296).

§ XIII. VOLATILE OILS. CAMPHENE. CAMPHOR. CAMPHORIC ACID.
CITRENE. OIL OF COPIVI.

THE *volatile* or *essential* oils are generally obtained by distilling the vegetables, or the parts of the plants which afford them, with water, in common stills; the water and oil pass over together, and are collected in the *Italian* recipient shown in the following cut, in which the water, having reached the level *a b*, runs off by the pipe *c*, and the oil, being generally lighter than water, floats upon its surface in the space *d*. The whole contents of the recipient are then poured into a funnel, the tube of which is closed with the finger; and when the oil has collected upon the surface, the water is suffered to run from it and the oil transferred into a bottle. The distilled water, being saturated with the oil, should be retained for a repetition of the distillation. The produce of oil is sometimes increased, by adding salt to the water in the still, so as to elevate its boiling point a few degrees.



Some of the volatile oils are obtained by expression, such as those of *lemon*, *orange*, and *bergamot*, which are contained in distinct vesicles in the rind of those fruits.

The volatile oils vary considerably in specific gravity, as shown by the following Table:—

Oil of Sassafras	1.094	Oil of Tansy	946
„ Cinnamon	1.035	„ Caraway	940
„ Cloves	1.034	„ Origanum	940
„ Fennel	997	„ Spike	936
„ Dill	994	„ Rosemary	934
„ Pennyroyal	978	„ Juniper	911
„ Cummin	975	„ Oranges	888
„ Mint	975	„ Turpentine	872
„ Nutmegs	948		

The *general* characters of these oils are the following: they have a penetrating odour and taste, and are generally of a yellowish colour; they are for the most part very soluble in alcohol, and very sparingly soluble in water; these solutions constitute *perfumed essences* and *distilled waters*. The latter are principally employed in pharmacy, and the former as perfumes. When pure, they pass into vapour at a temperature somewhat above that of 212°; but when distilled with water, they pass over at its boiling point. They are very inflammable, and water and carbonic acid are the results of their perfect combustion. As many of these oils bear a very high price, they are not unfrequently adulterated with alcohol and fixed oils. The former addition is rendered evident by the action of water; the latter, by the greasy spot which they leave on paper, and which does not evaporate when gently heated. By long keeping, some of the essential oils are concreted into a substance resembling spermaceti; this is especially the case with the ottar of rose, and sometimes appears

connected with the destruction of its odoriferous principle. When oil of aniseed is kept for many years it also loses its odour, and becomes entirely solid. Other oils become resinous by age. (MACCULLOCH, *Quarterly Journal*, N.S., v. 291.) The volatile oils absorb oxygen, when long exposed to it, and become thick and resinous. Nitric and sulphuric acids rapidly decompose the volatile oils: a mixture of 4 parts of nitric, and 1 of sulphuric acid, poured into a small quantity of oil of turpentine, produces instant inflammation. They absorb chlorine, and hydrochloric acid is produced, along with a peculiar substance, called artificial camphor. Iodine produces changes somewhat analogous. Hydrochloric acid combines with several of them, and forms a crystallizable compound which has also been compared to camphor. (See *Camphor*.)

The relative quantity of essential oils, furnished from different materials, is liable to much variation; the following are the average products of 1 cwt. of the different vegetable substances:—

		Ounces.	
Juniper-berries (common)		4	to 5
" " (fine Italian)		7	" 8
Aniseed (common)		32	" 33
" (finest)		36	" 33
		lbs.	oz.
Caraways	from	3	12
Dill-seed	"	2	0
Cloves	"	18	0
Pimento	"	2	0
Fennel-seed	"		2 0
Leaves of the <i>Juniperus sabina</i> .	"		0 14

The essential oils have recently been subjects of more interest to the chemist, from the results afforded by their ultimate analysis: these have shown that certain organic compounds, commonly arranged with the volatile oils, are binary compounds of carbon and hydrogen, or *hydrocarbons*: to these, allusion has already been made in the section on carbon, and we shall now have to consider them more in detail: others are binary compounds of carbon, hydrogen, and oxygen, or *oxides of hydrocarbon*, and two or three of them are of a more complex character, such as the oil of mustard-seed.

A. To the first class belong the oils of turpentine, of lemons, and of copivi balsam; these are hydrocarbons.

I. OIL OF TURPENTINE. CAMPHOGEN, OR CAMPHENE.—Oil of turpentine is one of the most important of these oils, in consequence of its numerous applications in the arts, especially in the manufacture of paints and varnishes. It is obtained by distilling *turpentine* with water, with the vapour of which it readily passes over at 212° , though its boiling-point exceeds 314° . It is very sparingly soluble in alcohol. By exposure to air a part of it is converted into resinous matter, and a part into a peculiar acid matter, which, when distilled, deposits a crystallizable substance, upon exposure to cold. (*Ann. de Ch. et Ph.*, xxxi. 442.) In consequence of the great inflammability of oil of turpentine, it is highly dangerous when kept in quantities. If preserved in wooden vessels they are very apt to leak, hence the necessity of placing them in another cask,

surrounded by water. In common oil of turpentine Dr. Ure found 82·35 carbon, 9·80 hydrogen, 7·85 oxygen: when purified by alcohol, the specific gravity of this oil was reduced from ·888 to ·878: it then appeared to be a binary compound of carbon and hydrogen, nearly resembling naphtha in composition. This suggestion, thrown out by Dr. Ure (*Phil. Trans.*, 1822), has since been verified by Dumas, who deprived it of all adhering water and acid, by agitating it with quicklime, subjecting it to a careful distillation, and finally digesting it with chloride of calcium. In this state its specific gravity is ·860, and its boiling point 312°. From the density of its vapour (4·763) Dumas infers that it contains, in the 100 volumes, 500 volumes of carbon vapour and 800 of hydrogen, and as

500	Cubic inches of carbon vapour weigh	131·5
800	„ hydrogen gas	17·0
100	„ of turpentine vapour	= 148·5

These weights bear the ratio to each other of 10 equivalents of carbon to 8 of hydrogen, or

Carbon	10	60	33·2	Dumas.	38·5
Hydrogen	8	8	11·3		11·5
Oil of turpentine	1	68	100·0		100·0

The calculated density of its vapour is 4·74; or,

5	Volumes of carbon vapour	= 0·840 × 5 = 4·20
8	„ hydrogen	= 0·068 × 8 = 0·54
		4·74

1. CAMPHOR.—This substance, which in many respects resembles the essential oils, being like them, volatile, inflammable, soluble in alcohol, and sparingly soluble in water, has been shown by Dumas to be an oxide of an hydrocarbon identical in composition with pure oil of turpentine; hence the term *Camphogen* or *Camphene*, applied to that oil. In its ordinary state camphor is white, semi-transparent, and concrete. Its specific gravity is ·98. It fuses at about 300° in close vessels, and rises rapidly in vapour. It dissolves in the fixed and volatile oils. It is scarcely acted upon by the alkalis; some of the acids dissolve, others decompose it. (CHEVREUL, *Ann. de Ch.*, LXXiii.) It dissolves in sulphuric acid, forming a brown solution, from which it is at first precipitated, unaltered, by water; sulphurous acid is afterwards evolved, the solution becomes black and thick, and, after some days, affords a brown coagulum on the addition of water, and smells fragrant and peculiar. On distilling the diluted liquor, water and a yellow oil pass over, a little sulphurous acid is then disengaged, and a black matter remains in the retort, which, when digested in alcohol, affords a portion of soluble matter having some of the properties of artificial tannin. (HATCHETT, *Phil. Trans.*, 1805.)

If mixed with bole or powdered clay, and repeatedly distilled, camphor is almost entirely converted into a liquid, having the characters of essential oil. It also furnishes a peculiar yellow oleaginous product, when its vapour is passed through a tube over red-hot iron; this product is, according to F. D'Arcet, a peculiar hydrocarbon. (*Ann. de Ch. et Ph.*, LXvi. 110.)

The camphor of commerce is obtained from the *Laurus camphora*, and comes chiefly from Japan. It is originally separated by distillation, and subsequently purified in Europe in a subliming-vessel somewhat of the shape of a turnip, from which the cakes of camphor derive their form. There are other trees and plants which afford it.

The specific gravity of the vapour of camphor is 5.29, which corresponds with

5 Volumes of carbon vapour	= 4.20
8 " hydrogen gas	= 0.54
$\frac{1}{2}$ " oxygen	= 0.55
5.29	

Hence, camphor appears to be the *protoxide of camphogen*, or to consist of

				Dumas.	Ure.
Carbon	10	60	79.0	79.28	78.02
Hydrogen	8	8	10.5	10.36	11.58
Oxygen	1	8	10.5	10.36	10.40
Camphor	1	76	100.0	100.00	100.00

2. CAMPHORIC ACID. — When camphor is repeatedly distilled with nitric acid, it is converted into *camphoric acid*. For this purpose, 4 ounces of camphor, reduced to powder by triturating it with a few drops of spirit of wine, may be introduced into a two-quart tubulated retort, placed in a sand-heat; pour upon it 30 ounces of common nitric acid, and proceed to slow distillation. When two-thirds of the acid have passed over, return it into the retort and distil as before, repeating the operation twice more; after which, as the liquor cools, a quantity of crystals of camphoric acid are deposited, which are to be washed and dried. This acid assumes the form of plumose crystals, soluble in about 100 parts of water at 60°, and in rather more than 1 part of alcohol. Its taste is acid, and somewhat acrid, and it has an aromatic odour. Exposed to heat, it sublimes unaltered. It combines with the salifiable bases, constituting a class of salts called *Camphorates*.

Camphoric acid, in its *anhydrous* state, is composed of

				Dumas.
Carbon	10	60	55.6	56.03
Hydrogen	8	8	7.4	7.32
Oxygen	5	40	37.0	36.65
Camphoric acid	1	108	100.0	100.00

The *crystallized* acid, according to Brandes, includes 1 atom of water: it appears, therefore, that camphoric acid is = (camphor + 40), or (camphogene + 50).

CAMPHORATES. — The neutral camphorates include 6 atoms of oxygen; namely, 1 in the base and 5 in the acid. They have a bitterish aromatic flavour, and are decomposed by the stronger acids. Subjected to destructive distillation they yield water, empyreumatic oil, and charcoal: in the air they burn with a blue or reddish flame. The camphorates of ammonia, potassa, and soda, are very soluble, deliquescent, and difficultly crystallizable; they are soluble in alcohol. The camphorates of baryta, lime,

strontia, magnesia, and manganese, are also soluble in water. If the camphor has not been perfectly acidified, the camphoric acid retains it in combination, and the salts are rendered much less soluble. The camphorate of peroxide of iron, of tin, zinc, lead, copper, uranium, protoxide of mercury and of silver, are insoluble, or nearly so.

3. HYDRATE OF OIL OF TURPENTINE. HYDRATE OF CAMPHOGEN.—Dumas has described, under this term, a crystalline compound, which is often found in mixtures of oil of turpentine and water; and, in cases where drops of water have adhered to the interior of bottles containing oil of turpentine, each drop has been found successively converted into a tuft of crystals. It is colourless, tasteless, and odourless, crystallizes in rhomboidal prisms forming stellated groups, and is heavier than water. It fuses and sublimes at temperatures of about 300° to 360° . It dissolves in 22 parts of boiling water, and crystallizes as the solution cools: alcohol and ether also dissolve it. Peligot and Dumas have observed the same compound in essential oil of cardamoms, and it is probably not an uncommon product. It consists of ($^{10}car + ^{11}h + ^3o$), or of

Camphogen	1	. . .	68	. . .	71.6
Water	3	. . .	27	. . .	28.4
<hr/>					
Hydrate of camphogen	1		95		100.0

4. HYDROCHLORATE OF CAMPHOGEN. ARTIFICIAL CAMPHOR.—This curious substance was discovered by Kind (*Ann. de Ch.*, li. 270); it is formed by slowly passing dry hydrochloric acid gas through oil of turpentine surrounded by ice, so as to keep down its temperature; the quantity of the product is very variable, but sometimes equals or exceeds that of the oil of turpentine employed, the oil absorbing a third of its weight of acid. The artificial camphor separates in the course of some hours. It is white, crystalline, of a peculiar and somewhat camphory odour, fusible below 212° , soluble in about 3 parts of pure alcohol, and deposited in crystals from a hot saturated solution. It is volatile, but not without decomposition, for when sublimed in a retort a little hydrochloric acid is always formed: it is decomposed by lime, and the oil evolved unaltered in its composition.

The mother-liquor, from which this hydrochlorate is deposited, is fuming, pungent, and lighter than water: when distilled, it yields a clear yellow oil, and leaves a brown residue. (BLANCHET and SELL, *Jour. de Phar.*, xx. 224.) Hydrochlorate of camphogen consists of ($^{20}car + ^{17}h + ^1c$), or

Camphogen	2	. . .	136	. . .	78.6
Hydrochloric acid	1	. . .	37	. . .	21.4
<hr/>					
Hydrochlorate of camphogen	1		173		100.0

II. ESSENTIAL OIL OF LEMONS. CITRENE.—This oil is generally obtained by expression, from the exterior rind of the fruit of the lemon. (*Citrus medica*.) It is also obtained by distillation. In the former case the oil is extremely fragrant, but somewhat turbid, and liable to change in consequence of the presence of a little mucilage: the distilled oil is perfectly limpid and permanent,

Essence of lemons, when pure, is colourless, limpid, and very fragrant. Its specific gravity is 0·847 at 70°. It dissolves in all proportions in anhydrous alcohol, but 100 parts of alcohol, of specific gravity ·837, only dissolve about 15 parts. It consists, according to the analysis of Dumas, of carbon and hydrogen in the same relative proportions as in oil of turpentine, but they are one-half less condensed, so that it may be represented by ($5\text{ car} + 4\text{ h}$), or

Carbon	5	30	88·2	Dumas.
Hydrogen	4	4	11·8	11·5
Essence of lemons	1	34	100·0	100·0

The essential oils of bergamot, of cedrato, and probably of orange, are similarly composed.

1. HYDROCHLORATE OF CITRENE.—An artificial camphor may be obtained from essence of lemons by the same process as that applicable to essence of turpentine. Blanchet and Sell (*Jour. de Phar.*) regard the essence of lemons (as also that of turpentine) as a mixture of two distinct hydrocarbons, one of which yields the crystallizable camphor, and the other the uncrystallizable fuming mother-liquor; to these they have applied the terms *citronyle* and *citryle*. According to Dumas, the crystallizable product is white, lamellar, or nacreous, fusible at 105°, and concretes into a brilliant mass on cooling. It consists of ($10\text{ car} + 9\text{ h} + \text{c}$), or

Citrene	2	68	64·8
Hydrochloric acid	1	37	35·2
Hydrochlorate of citrene	1	105	100·0

III. OIL OF COPIVI.—The *balsam of copivi*, which is an exudation resembling turpentine, from several species of *Copaifera*, yields, when distilled, a peculiar fragrant volatile oil, which, when deprived of water by digestion with chloride of calcium, has a specific gravity=0·878: absolute alcohol dissolves two-fifths its weight of it, and it is soluble to any extent in ether and in sulphuret of carbon: it dissolves sulphur and phosphorus, and absorbs chlorine, which renders it viscid; when dropped upon iodine, heat and hydriodic acid are evolved. It forms, with hydrochloric acid, a compound analogous to artificial camphor, and also a fuming liquid. This oil, according to Blanchet, corresponds in composition and in atomic constitution with the oil of lemon.

B. The second class of essential oils, or those which are *oxides of hydrocarbon*, includes the greater number of those products: their real nature is, as yet, but imperfectly understood, but it is highly probable they are solutions of a substance analogous to camphor in liquid hydrocarbons, and that they may, therefore, be atomically represented by $(\text{car} + \text{h}) + (\text{car} + \text{h} + \text{o})$. Some of these oils, when exposed to cold, yield crystalline deposits, which are modifications of camphor, or solid oxides of hydrocarbon: those from oil of peppermint and oil of aniseed have been examined by Dumas, and several others have been noticed and analyzed; the deposit from oil of roses, oil of sassafras, oil of *cinnamon*, (DUMAS and PELIGOT, *Ann. de Ch. et Ph.*, lvii. 311,) and many others,

which are gradually deposited, or formed by the action of air, are probably of the same nature. Such of these oils as are most dense, are, according to Dumas, most highly oxidized; some of these pass into *resins*, and others exhibit a tendency to combine with bases; this is especially the case with *oil of cloves* and *pimento*. (BONASTRE, *Jour. de Phar.*, xiii.) According to Dumas, the composition of *oil of cloves* may be represented by ($^{20}car + ^{13}h + ^5o$), giving an equivalent = 173, and combining, in this proportion, with an equivalent of ammonia; so that 173 oil of cloves + 17 ammonia would form 190 of *caryophyllate of ammonia*. The crystalline deposit from oil of cloves which has been long kept, is stated by Dumas to be not only analogous to, but identical with, camphor.

§ XIV. BENZULE. BENZOIC ACID. AMYGDALINE. CINNAMULE.

AMONGST the essential oils, that which is obtained by distilling the cake which remains after the fixed oil has been expressed from bitter almonds, is perhaps the most interesting. In its ordinary state, this oil is a mixture of hydrocyanic acid, and a peculiar volatile oil, neither of which pre-exist in the almond, but are produced by the action of heat and water, during the distillation, upon a peculiar principle contained in the almond, and which has been termed *amygdaline*. (*Nouvelles Expériences sur les Amandes Amères, et sur l'Huile Volatile qu'elles fournissent, par ROBIGNET et BOUTRON-CHARLARD, Ann. de Ch. et Ph.*, xlv. 352.) The essential oil may be separated from the hydrocyanic acid, by agitating it with a solution of potassa and protochloride of iron, and subjecting it to distillation; and it may then be deprived of adhering water, by redistilling it over quick-lime. (WÖHLER and LIEBIG, *Ann. de Ch. et Ph.*, li. 273.)

When thus purified, that is, deprived of hydrocyanic acid and water, the essential oil is clear and colourless, and its odour resembles that which it originally possessed: its flavour is hot and aromatic; its sp. gr. = 1.043. It is very sparingly soluble in water, but alcohol dissolves it in all proportions. It is inflammable, but it may be passed, without decomposition, through a red-hot tube. Exposed to air, or other source of oxygen, it is converted into *crystallized benzoic acid*, and this conversion is extremely rapid under the direct influence of solar light. Exposed to the joint action of air, water, and a solution of potassa, *benzoate of potassa* is formed; and if the experiment be made over mercury, the ascent of the mercury indicates the absorption of the oxygen. It is not altered by the anhydrous alkalis; but when heated with *hydrate of potassa* out of the contact of air, benzoate of potassa is formed, and hydrogen evolved.

It has been shown by Liebig and Wöhler, that the atomic constitution of this oil is such, that it may be regarded as the *hydruret* of a base composed of carbon, hydrogen, and oxygen, which base cannot be isolated, but may be transferred, without decomposition, from one combination to another, in the same manner as cyanogen. Combined with oxygen, this base produces *benzoic acid*; hence they have termed it *benzule*.

BENZULE is represented by ($^{14}car + ^5h + ^2o$): or it consists of

Carbon	14	84	80.00
Hydrogen	5	5	4.76
Oxygen	2	16	15.24
Benzule	1	105	100.00

HYDRURET OF BENZULE is the above-mentioned purified oil of bitter almonds, deprived of hydrocyanic acid, in which state it consists of (BEN + *h*), or $105 + 1 = 106$: its ultimate composition being

				Dumas.
Carbon	14	84	79.2	79.57
Hydrogen	6	6	5.7	5.56
Oxygen	2	16	15.1	14.87
Hydruret of benzule	1	106	100.0	100.00

CHLORIDE OF BENZULE.—When chlorine is passed through the above hydruret, it is absorbed, heat and hydrochloric acid are evolved, it becomes yellow, and when no more hydrochloric acid is formed, the liquid is heated; it becomes limpid and colourless, and is then pure *chloride of benzule*; its sp. gr. is 1.196: its odour is pungent and irritating, its boiling-point high, and it burns with a greenish sooty flame: when poured into water it falls to the bottom, where it remains insoluble; but by boiling, it forms crystallized benzoic acid and hydrochloric acid. It may be heated with baryta and lime without decomposition, but with hydrate of potassa it yields chloride of potassium and benzoate of potassa. It dissolves phosphorus and sulphur, with the aid of heat, but deposits them in crystals as the solutions cool. With the solid chloride of phosphorus it evolves heat, produces the liquid chloride, and an oily compound of a penetrating odour. It dissolves in alcohol, and the solution soon becomes so hot as to enter into ebullition, hydrochloric acid is evolved, and on the addition of water benzoic ether separates.

Chloride of benzule is represented by (BEN + *c*), or $105 + 36 = 141$. It consists, therefore, of

				Dumas.
Carbon	14	84	59.57	60.02
Hydrogen	5	5	3.55	3.51
Oxygen	2	16	11.35	11.55
Chlorine	1	36	25.53	24.92
Chloride of benzule	1	141	100.00	100.00

IODIDE OF BENZULE is formed by distilling iodide of potassium with chloride of benzule: it passes over as a brown liquid, which concretes on cooling, and which, when freed from mixed iodine, is a white crystalline solid: it consists of (BEN + *i*), or $105 + 126 = 231$.

BROMIDE OF BENZULE is produced by the direct action of bromine on the hydruret of benzule: it is brown, crystalline, soluble in alcohol and ether, and by continued ebullition with water is converted into benzoic and hydrobromic acids. It is represented by (BEN + *b*), or $105 + 78 = 183$.

SULPHURET OF BENZULE is formed by distilling chloride of benzule with finely-powdered sulphuret of lead: it distils over in the form of an

oily fluid, which concretes into a yellow crystalline mass: it smells of sulphur; water does not affect it, but when boiled with a solution of potassa, benzoate and hydrosulphuret of potassa are formed. This compound is represented by $(\text{BEN} + \text{S})$, or $105 + 16 = 121$.

CYANURET OF BENZULE.—When chloride of benzule is distilled off cyanuret of mercury a yellow oil passes over, and chloride of mercury remains in the retort. When the liquid is rectified it is colourless, but soon becomes yellow; it has a pungent irritating odour, a biting and sweetish flavour, which a little resembles that of oil of cinnamon. It is denser than water, and is converted by its action into benzoic and hydrocyanic acids: it burns with a white fuliginous flame: its symbol is $(\text{BEN} + \text{Cy})$, or $105 + 26 = 131$. The ultimate elements of this curious compound are

Carbon	16	96	73.5
Hydrogen	5	5	3.6
Oxygen	2	16	12.2
Nitrogen	1	14	10.7
<hr/>					
Cyanuret of benzule	1		131		100.0

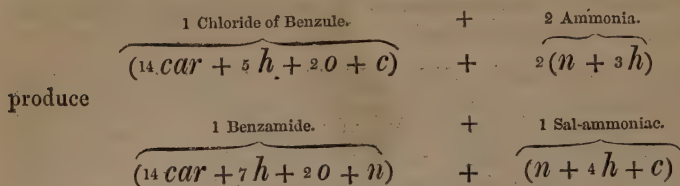
BENZAMIDE.—Dry ammoniacal gas is rapidly absorbed by chloride of benzule, heat is evolved, and a white crystalline solid formed, consisting of sal-ammoniac, in combination with a new substance called by Liebig and Wöhler *Benzamide*, from its analogy to oxamide. When the product is first washed in cold water, and then dissolved in boiling water, the benzamide crystallizes as the solution cools. Benzamide is also formed during the mutual action of hippuric acid and binoxide of lead; when they are boiled together in water, carbonic acid is evolved, and hippurate of lead and benzamide remain in solution. Sulphuric acid (not in excess) is then added, and the whole again boiled with a fresh portion of the binoxide, and this operation is repeated till the whole of the hippuric acid is decomposed; the liquid, when freed from lead, yields crystals of benzamide on evaporation.

Benzamide fuses at 240° into a limpid liquid, which concretes into a foliated mass: at a higher temperature it boils, and distils over unaltered: its vapour burns with a smoky flame. It dissolves in alcohol, and in hot ether. Triturated with caustic potassa it evolves no ammonia, but when boiled in caustic potassa, ammonia is evolved and benzoate of potassa formed. Boiled with sulphuric acid, benzoic acid sublimes, and sulphate of ammonia is formed. The ultimate elements of *benzamide*, regarding it as a compound of *benzule* and *amidé*, are $(14 \text{ car} + 5 \text{ h} + 2 \text{ o}) + (n + 2 \text{ h})$, or $105 + 16 = 121$, and may therefore be thus represented:—

						Dumas.
Carbon	14	84	69.5	69.73
Hydrogen	7	7	5.8	5.69
Oxygen	2	16	13.2	13.05
Nitrogen	1	14	11.5	11.53
<hr/>						
Benzamide	1		121		100.0	100.00

Hence, the action of ammonia on chloride of benzule is such, that

1 atom of the chloride, and 2 atoms of ammonia, produce 1 atom of sal-ammoniac, and 1 atom of benzamide: or,



BENZINE, or BENZOINE.—This substance, known under the name of *camphor* of essence of bitter almonds, is produced in the form of a crystalline deposit, when the oil is left for some weeks in contact with a strong solution of potassa; it may be purified by solution in hot alcohol and filtering through animal charcoal: as the alcoholic solution cools it forms prismatic crystals, fusible at 248° , tasteless and inodorous, and coinciding with the original oil (hydruret of benzule) in composition. (WÖHLER and LIEBIG.)

BENZOIC ACID. (BEN + O.)—This acid has lately acquired much interest to the theoretical chemist, in consequence of its relation to the compound radical or base which I have just described under the name of *Benzule*, and of which it is, in fact, an oxide. Benzoic acid exists ready-formed, in benzoin, which is the resinoid exudation of the *styrax benzoe*, whence its name; it is found also in some of the *balsams**, and is produced by the action of heat, acids, and alkalis, on amygdaline, benzamide, and hippuric acid; lastly, it is formed by the action of oxygen on the hydruret of benzule, above described.

Benzoic acid is usually obtained by heating benzoin in a convenient vessel or apparatus, such as a crucible, with a cone of paper attached to its mouth; the acid condenses in it in fine acicular crystals, which were formerly called *flowers of benzoin*. A good process for procuring this acid is that recommended by Mr. Hatchett, which consists in digesting benzoin in sulphuric acid, when it affords, on the application of heat, a copious sublimate of pure benzoic acid. (*Additional Experiments on Tannin, Phil. Trans.*, 1808.) It may also be obtained by boiling a pound and a-half of powdered benzoin with 4 ounces of quick-lime, in 6 or 8 quarts of water. When cold, the clear liquid is decanted, and the residuum again boiled in half the former quantity of water. The liquors thus obtained are boiled down to half their bulk, filtered, and mixed with hydrochloric acid, as long as it occasions a precipitate, from which the liquor is poured off, and, when dry, it is put into an earthen vessel placed in a sand heat, and sublimed into paper cones.

In making benzoic acid upon a large scale, by the process of sublimation, the better kind of benzoin is most economically employed: it may be put into an iron pot, set in brickwork over a proper fire-place; the sublimate is most conveniently received into a large wooden box

* The balsams of Tolu and of Peru have generally been regarded as containing benzoic acid; but, according to Fremy (*Ann. de Ch. et Ph.*, LXX. 180), they contain cinnamic acid.

lined with paper, communicating by a conical iron or tin-plate neck with the subliming pot. The first product may be sublimed a second time in the same apparatus; and, by conducting the process rather rapidly, the acid condenses in beautiful acicular crystals, somewhat elastic. If slowly sublimed, it is more scaly. By this process of sublimation, good benzoin yields 10 to 12 per cent. of acid contaminated by empyreumatic oil, and which, when pressed between folds of blotting-paper, and again sublimed, is reduced to the proportion of 8 or 9 per cent. of the purified acid*.

Benzoic acid, when it has been thus sublimed, is in the form of plumose or acicular crystals, inflammable, fusible at 230° , and boils at 460° ; it is light, of an aromatic and slightly sour taste, soluble in 25 or 30 parts of boiling water, and in 200 of cold water. It is much more soluble in alcohol; and this solution easily furnishes it pure, and in prismatic crystals. It is soluble, without immediate change, in nitric and sulphuric acids, and in many other acids by the aid of heat. The oils also dissolve it. When the vapour of benzoic acid is passed over red-hot iron, it is converted into carbonic acid, and a peculiar oil is formed, which has been examined by F. D'Arcet. (*Ann. de Ch. et Ph.*, LXVI. 99.) According to this chemist, the oil is a hydrocarbon composed of $24\text{ car} + 12\text{ h}$, which $+ 2\text{ car}'$, constitute benzoic acid. But these atomic views are not consistent with those generally adopted.

According to Dumas and Mitscherlich, the density of the vapour of benzoic acid is 4.27. Anhydrous benzoic acid may be represented by (BEN + O), that is, as an oxide of benzule; or $105 + 8 = 113$: its ultimate components therefore are,

	Dumas.			
Carbon	14	84	74.3	74.7
Hydrogen	5	5	4.4	4.3
Oxygen	3	24	21.3	21.0
Anhydrous benzoic acid	1	113	100.0	100.0

The *crystallized* acid contains 1 equivalent of water, and is represented by (*ben* + *q*), or $113 + 9 = 122$. The water cannot be expelled by heat, and is contained in most of the *benzoates*. The *benzoate of silver* is anhydrous.

BENZOATES.—In the neutral anhydrous benzoates, the oxygen in the acid is to that in the base as 3 to 1: these salts are easy of decomposition, and their solutions give a precipitate of benzoic acid with the stronger acids: they give a dingy-red precipitate with the persalts of iron. Many

* According to Stoltze, good benzoin should yield 12 or 13 per cent. of pure acid by the process of sublimation; and 18 per cent. by the following process: Dissolve 1 part of benzoin in 3 of alcohol; neutralize the solution with carbonate of soda dissolved in a mixture of 8 parts of water and 3 of alcohol: add to the mixture 2 parts of water, and distil off the alcohol: decant the residuary liquid from the resinous deposit, and decompose it by sulphuric acid.

Benzoic acid is also made by evaporating the urine of cows, horses, &c., precipitating the hippuric acid by hydrochloric acid, and decomposing this product by nitric acid: it obstinately retains an urinous odour, which may be covered by mixing it with about a twentieth part of benzoin, and subliming. (See *Urine*.) In some cases, benzoic acid may be economically prepared by subjecting essence of bitter almonds to the action of the air.

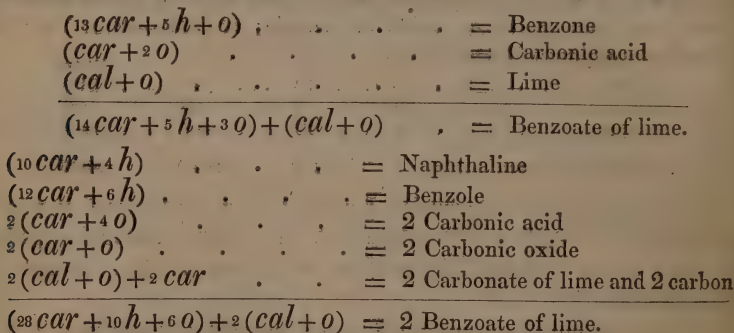
of the benzoates which are not soluble in water are soluble in hot solutions of acetate of potassa and soda, and in nitrate of soda; but they are insoluble in nitrate of potassa, and in the sulphates of potassa and soda.

BENZOATE OF AMMONIA forms deliquescent plumose crystals, very soluble in water. Berzelius recommends this salt as a precipitant of peroxide of iron, which it throws down of an orange-red colour. Crystallized benzoate of ammonia consists, according to Thomson, of 1 proportional of acid, 1 of base, and 1 of water.

BENZOATE OF POTASSA (*ben* + P + *q*) is a very soluble deliquescent salt; if it be digested with benzoic acid, a *bibenzoate of potassa* results, which, according to Bucholz (*Ann de Ch.*, LXXXIV.), forms acicular and lamellar crystals, requiring 10 parts of water for their solution.

BENZOATE OF SODA forms efflorescent crystals, very soluble in water.

BENZOATE OF LIME forms acicular crystals, sparingly soluble in cold water. Vauquelin found this salt in the urine of the cow. Benzoate of ammonia forms a copious white precipitate when added to solution of chloride of calcium, which is soluble in hot water. When benzoate of lime is subjected to destructive distillation, it yields two fluid products, namely, *Benzene* ($^{13}car + ^5h + o$) and *Benzole* ($^{12}car + ^6h$). Naphthaline is also at the same time formed, carbonic oxide is evolved, and carbon and carbonate of lime form the residue. (PELIGOT.) The following formulæ, illustrative of these decompositions, are given by Liebig:—



BENZOATE OF BARYTA is soluble and crystallizable.

BENZOATE OF STRONTIA is also a soluble salt.

BENZOATE OF MAGNESIA forms soluble plumose crystals.

BENZOATE OF MANGANESE forms beautiful prismatic crystals, which are soluble in 20 parts of cold water, and in alcohol.

BENZOATE OF IRON.—Benzoate of ammonia forms an insoluble *perbenzoate* when added to solutions of peroxide of iron, of a reddish colour: in the protosalts of iron, it forms a white precipitate.

BENZOATE OF ZINC forms soluble acicular crystals when there is excess of acid: the neutral benzoate is insoluble.

BENZOATE OF TIN is insoluble, or nearly so, in water.

BENZOATE OF COPPER is a fine blue compound, difficultly soluble in water, but soluble in excess of benzoic acid, and insoluble in alcohol.

BENZOATE OF LEAD is insoluble, except there be excess of acid; it then forms nacreous crystals.

BENZOATE OF ANTIMONY has not been examined.

BENZOATE OF BISMUTH forms white acicular crystals, permanent in the air, soluble in water, and sparingly soluble in alcohol. (TROMMSDORF, *Ann. de Ch.*, xi.) When benzoate of ammonia is added to acid nitrate of bismuth, it forms an insoluble white precipitate; Trommsdorf's salt therefore is probably a *bibenzoate*.

BENZOATE OF COBALT.—Benzoate of ammonia forms no precipitate in solutions of cobalt.

BENZOATE OF URANIUM is a difficultly soluble straw-coloured compound, formed by adding benzoate of ammonia to nitrate of uranium.

BENZOATE OF NICKEL.—Solutions of nickel are only rendered slightly turbid by benzoate of ammonia; benzoate of nickel is probably therefore a soluble salt.

BENZOATE OF MERCURY.—Benzoic acid forms white precipitates in the solutions of mercury.

BENZOATE OF SILVER, obtained by digesting moist oxide of silver in benzoic acid, forms acicular crystals; but benzoate of ammonia produces an abundant insoluble precipitate in solution of nitrate of silver. This salt is *anhydrous*, and consists of 116 oxide of silver + 118 benzoic acid.

BENZOATE OF ALUMINA forms arborescent crystals.

AMYGDALIN.—This curious substance, discovered by Robiquet and Boutron-Charlard, is obtained as follows:—Bitter almonds are powdered and subjected to powerful pressure to separate the greater part of the fixed oil: the residuary cake is powdered and repeatedly boiled in alcohol (of 93 to 94 per cent.), and the solutions thus obtained are mixed and distilled in a water bath till the alcohol has passed over: the viscid liquid which remains is then diluted with water, a little ferment added, and the mixture kept in a warm place, when fermentation ensues; when this has ceased, the liquid is filtered, evaporated in a water-bath to the consistence of syrup, and mixed with alcohol, by which amygdalin is thrown down in the form of a white crystalline powder which requires to be purified by a second solution and crystallization. About 4 or 5 per cent. of amygdalin are thus obtained from the cake.

Amygdalin forms small crystalline grains, inodorous, and slightly tasting of bitter almonds: it is scarcely soluble in alcohol, very soluble in water, from which it may be obtained in prismatic hydrated crystals. When distilled with dilute nitric acid, it is resolved into hydruret of benzule, ammonia, and benzoic, formic, and carbonic acids. The fixed alkalis convert it into amygdalic acid and ammonia. Its ultimate constituents are:—

Carbon	40	240	52·98
Hydrogen	27	27	5·83
Oxygen	22	176	38·13
Nitrogen	1	14	3·06
Amygdalin	1	457	100·00

When amygdalin in cold aqueous solution is mixed with *emulsin**, it suffers decomposition, and hydrocyanic acid and hydruret of benzule are immediately formed: hence it is, that no hydrocyanic acid or volatile oil can be discovered in the bitter almond till it is wetted, as when chewed or triturated with cold water into an emulsion: if boiling water be used, the emulsin is coagulated and no hydrocyanic acid or hydruret of benzule is formed, so that to obtain those products, the marc or cake must be digested in water below 140°, and then distilled. A peculiar form of sugar and formic acid are also results of the mutual action of amygdalin and emulsin. According to Liebig and Wöhler (*Handwörterbuch der Chemie*), 1 atom of amygdalin includes the elements of

	Atoms of			
	Carbon.	Hydrogen.	Oxygen.	Nitrogen.
1 atom of hydrocyanic acid	2	1	0	1
2 atoms of hydruret of benzule	28	12	4	0
1 atom of sugar	6	7	7	0
1 atom of formic acid	4	2	6	0
5 atoms of water	0	5	5	0
1 atom of amygdalin	40	27	22	1

AMYGDALIC ACID.—This is the product of the action of caustic alkalis upon amygdalin: it may be obtained by boiling amygdalin in baryta water; ammonia is evolved, and *amygdalate of baryta* remains in solution; this may be decomposed by the due addition of dilute sulphuric acid, and on evaporating the filtered solution an imperfectly crystalline residue is obtained, which becomes gumlike when dried, is very soluble in water, deliquescent, insoluble in cold, and very sparingly soluble in boiling alcohol: its aqueous solution is slightly sour. When this acid or its salts are heated with sulphuric acid and black oxide of manganese, carbonic acid, formic acid, and hydruret of benzule are formed.

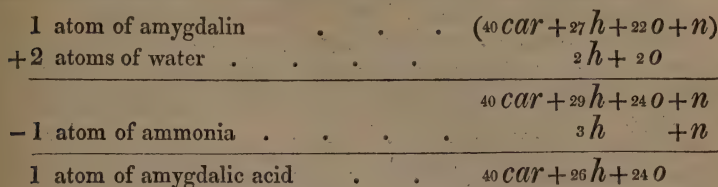
The ultimate elements of anhydrous amygdalic acid are:—

					Liebig.
Carbon	40	240	52·4		52·879
Hydrogen	26	26	5·7		5·613
Oxygen	24	192	41·9		41·508
Anhydrous amygdalic acid	1	458	100·0		100·000

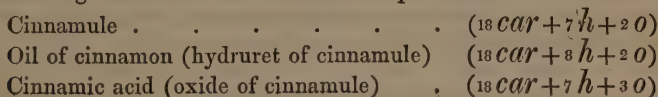
* This term has been applied to a principle which constitutes the greater part of the sweet and bitter almond: Robiquet has called it *Synaptase*. It is soluble in water and precipitated by alcohol in white flocks, which are again soluble in water. It is not precipitated by acids or oxide of lead: at 140° it coagulates like albumen. The *bitter* almond consists chiefly of amygdalin,

emulsin, and fixed oil, and so long as water is not present the amygdalin and emulsin cannot react on each other. When the bitter almond cake (which has been deprived by pressure of the greater part of its fixed oil) is digested in alcohol, the amygdalin is dissolved and the emulsin coagulated. Emulsin is a modified albumen; it disengages ammonia when acted on by caustic alkalis.

This acid is formed by adding the elements of 2 atoms of water to, and abstracting those of 1 atom of ammonia from amygdalin, for



CINNAMULE.—This term has been applied by Dumas and Peligot to the hypothetical radical of oil of cinnamon, and of the crystals which form in it when long exposed, and which they have called *cinnamic acid*: the following are the formulæ of these compounds:—



§ XV. RESINS. AMBER. CAOUTCHOUC.

THE RESINS are solid substances, which often exude spontaneously from trees and plants, or are extracted from other products by the agency chiefly of alcohol, in which they are more or less easily soluble*. They are insoluble in water; and their alcoholic solutions, when mixed with water, are rendered turbid and deposit the resin; their specific gravity varies from 0.92 to 1.20. They are brittle, and generally without much smell or taste, nonconductors of electricity, and rendered negatively electrical when rubbed. The resins fuse when heated, and are not, in their natural state, crystallizable. Some are more readily soluble in cold alcohol than others†, and some include two or more distinct species of resin: many of them contain essential oil, which they lose by

* The resins, as they exude from trees, are often mixed with *gum*, when they form *gum resins*, which are consequently only partially soluble in water and in alcohol; they readily dissolve in alkaline solutions when assisted by heat; and the acids act upon them nearly as upon the resins. *Ammoniacum*, *gamboge*, *assafoetida*, and *olibanum*, may be taken as examples of gum resins.

† *Copal*, *mastich*, and a few other resins, are very difficultly soluble in alcohol, and contain a substance which remains in the form of a viscid matter after the resinous portion has been separated by alcohol. Copal requires peculiar management to effect its solution in alcohol. A piece suspended in the vapour of boiling alcohol is gradually softened, and, as it drops down, dissolves in the

alcohol; camphor also accelerates its solution both in alcohol and in oil of turpentine. The most useful copal varnishes are those in which it is dissolved by the aid of a high temperature in linseed oil and turpentine.

Guaiacum is characterized by the singular changes of colour, which its alcoholic solution suffers when exposed to the action of nitric acid. (*Phil. Trans.*, 1811.) *Guaiacum* is also rendered blue by the gluten of wheat, but its colour is not changed by starch; the intensity of the blue colour is said to be proportional to the quantity of gluten present in flour. (TADDEI, *Giornale di Fisica*, i. 168. *Quarterly Journal*, vii. 376.) M. Pagenstecher has employed tincture of guaiacum, in conjunction with hydrocyanic acid, as a test of the presence of copper. (*Quart. Journal*, x. 182.)

exposure to air, or which may be abstracted from them by distillation. Some of them are soluble in sulphuric acid, without decomposition*, and are again thrown down by water. When heated, these solutions evolve sulphurous acid, and a carbonaceous deposit ensues, which contains artificial tan. They are generally decomposed by nitric acid, or considerably modified by its action. Some of them are soluble in hydrochloric and in acetic acids.

They combine with alkalis and salifiable bases, and form a class of compounds first studied by Hatchett, and subsequently by Unverdorben and others: in these compounds the resin performs the part of a weak acid: the resins are of great use in the arts: they constitute the basis of *varnishes*†, and of many plasters and cements.

COLOPHONY, or common *resin*, is the residue of the distillation of turpentine: the oil, or essence of turpentine, passes over, and the residue is a soft yellow substance, which hardens by exposure to air, and is known as *white or yellow resin*: when melted it loses water, and concretes on cooling into *black* or common resin (fiddler's rosin). The ultimate composition of this substance may be represented by oil of turpentine + oxygen; it is a compound of

Gay Lussac and Thenard.	
Carbon	75.944
Hydrogen	10.719
Oxygen	13.337
<hr/>	
100.000	

PINIC ACID.—According to Unverdorben (*Poggend.*, xi. 47), when colophony is digested in cold alcohol .833 specific gravity, a portion only is dissolved; the solution thus obtained, when mixed with an alcoholic solution of acetate of copper, yields a precipitate of *pinate of copper*; this precipitate, when washed with pure alcohol and digested in a mixture of alcohol and hydrochloric acid, furnishes a solution from which water throws down the *pinic acid*; when washed and boiled in water, it forms on cooling a hard brittle substance, which becomes brown by fusion, passing into what Unverdorben calls *colophonie acid*. When fused with the alkaline carbonates it expels their carbonic acid; and its ethereal solution decomposes carbonate of copper with effervescence. The *pinates of ammonia, soda, and potassa*, are soluble in water: those of the other bases, insoluble; the pinates are mostly insoluble in alcohol, but soluble in ether.

SILVIC ACID.—The resinous residue just mentioned as insoluble in cold alcohol, is soluble in boiling alcohol; and when this solution is mixed with a little sulphuric acid, it yields, on cooling, flat prismatic crystals of *silvic acid*: these two acids constitute nearly the whole of the resin, and according to Rose, (*DUMAS, Ch. app. aux Arts*, v. 688,) they are *isomeric*; they both consist of

* The properties of the resins have been ably investigated by Mr. Hatchett, the details of whose researches will be found in his communications to the Royal Society, printed in the *Philosophical Transactions* for 1804, 1805, 1806. They have more lately formed the subject

of a series of elaborate researches by Professor Johnston of Durham. (*Phil. Trans.*, 1839 and 1840.)

† The manufacture of varnishes would be irrelevant to this work; there is an excellent article on the subject in *AIKIN'S Chemical Dictionary*.

				Rose.
Carbon	40	240	79.0	79.28
Hydrogen	32	32	10.5	10.36
Oxygen	4	32	10.5	10.36
	1	304	[100.0	100.00

Silvic acid is insoluble in water, fusible at about 212° , soluble in alcohol and ether, and in sulphuric acid; but when its sulphuric solution is decomposed by water, the precipitate has the properties of *pinic acid*. The *silvates* of potassa, soda, and ammonia, are soluble in water; the *silvates* of the other bases are insoluble, but they mostly dissolve in alcohol and in ether: the *silvate of magnesia*, especially, is soluble in alcohol. The alcoholic solution of silvic acid yields a precipitate in an alcoholic solution of acetate of lead: the *silvate of lead* is a white fusible powder. When alcoholic solutions of silvic acid and nitrate of silver are mixed, no precipitate falls; but on the addition of ammonia a white powder is thrown down, which is *silvate of silver*. It is soluble in alcohol and in excess of ammonia.

The decomposition of resin for the purpose of obtaining an illuminating gas has already been adverted to. The products of this decomposition have been examined by Pelletier and Walter. (*Ann. de Ch. et Ph.*, LXVII. 269.)

LAC is a most useful substance: it has already been mentioned as a source of a dye stuff. It may be bleached by chlorine, and then forms an excellent varnish. It is also the basis of sealing-wax. *Red wax* is made by carefully fusing together 48 parts of shell-lac, 19 of Venice turpentine, 1 of Peru balsam, and 32 of fine cinnabar. *Black wax* is coloured with lamp-black: *yellow* with chromate of lead: *blue* with smalt: *green* with carbonate of copper.

AMBER.—This substance is commonly regarded as an antediluvian or fossil resin; it is chiefly brought from the southern coast of the Baltic, and is thrown up upon the beach between Königsberg and Memel: it also occurs in beds of brown coal, and of bituminous wood. It is transparent, or translucent, and of various shades of yellow and brown: its sp. gr. fluctuates between 1.06 and 1.07. It is considered by Berzelius as a mixture of two resins, bitumen, volatile oil, and succinic acid. When heated it fuses and burns, exhaling a peculiar and somewhat aromatic odour. It is used for various ornamental purposes; it is the basis of an excellent varnish, but it requires peculiar management to effect its solution either in oils or alcohol: *oil of amber* is used in medicine; but amber is chiefly interesting to the chemist as the source of *succinic acid*, which is exclusively obtained from it, though traces of the same acid are also found in the resins of the *conifera*.

SUCCINIC ACID.—The small pieces of amber which are inapplicable to ornamental purposes are used by the manufacturers of varnish, and as for this purpose the amber is heated or fused, a portion of acid and oil may be obtained from it. The common process for the preparation of succinic acid consists in subjecting amber to destructive distillation in a proper apparatus; it fuses, and then a yellowish aqueous fluid, containing acetic acid, goes over, followed by empyreumatic oil and succinic acid, part of

which concretes in the receiver. When the matter in the retort suddenly subsides, the process may be stopped, for a thick dark-coloured oil would follow, which would soil the other products; and ultimately a yellow waxy matter would rise, which is yielded by most of the resins, and which has not been particularly examined. Amber is apt to be adulterated, when in small fragments, with pieces of copal, but when it is genuine, 16 ounces of it yield about half an ounce of acid, 3 ounces of oil, and 10 ounces of torrefied resin, fit for amber varnish. When the *acid* is the only object of the operation, Julien recommends coarsely powdering the amber, and mixing with it, previous to distillation, one-twelfth part of sulphuric acid diluted with an equal weight of water; about twice as much acid, he says, will thus be obtained as when the amber is merely heated alone. (*Ann. of Phil.*, ii. 76.) Succinic acid may also be obtained by digesting amber in a solution of potassa, but the succinate of potassa so formed is contaminated by other soluble parts of the amber; it shows, however, that the succinic acid exists ready formed in the amber, and that it is not, as formerly supposed, an exclusive product of destructive distillation.

The acid, as at first produced, may be purified by dissolving it in twice its weight of nitric acid, and evaporating it to dryness in a retort; a little adhering nitric acid may be washed away by ice-cold water, and pure succinic acid remains. Richter recommends, for the purification of this acid, the saturation of the sublimed product with potassa, and ebullition with powdered charcoal; the solution is then filtered, and nitrate of lead added: the resulting insoluble *succinate of lead* is decomposed by the requisite addition of dilute sulphuric acid, and the solution of succinic acid thus obtained, being carefully evaporated, affords colourless prismatic crystals of the pure acid.

When succinic acid is obtained in the form of crystals from its aqueous solutions, it is in a *hydrated* state; its specific gravity is 1.55; its taste feebly acid; it is soluble in 3 parts of boiling and about 5 of cold water; it is scarcely soluble in cold alcohol, but boiling alcohol dissolves it more freely; it is almost insoluble in oil of turpentine, by which it is distinguished from benzoic acid. It is not decomposed by chlorine, nor by nitric or sulphuric acid; it is fusible and volatile, and not decomposed by sublimation: its fusing-point is high, and when it is sublimed it loses a part, but not the whole of its water.

The substances chiefly employed for the falsification of this acid, are, according to Dumas, tartaric acid, bisulphate of potassa, and sal-ammoniac: tartaric acid is discovered by the carbonaceous residue which it leaves when heated; the sulphate, by its want of volatility; and sal-ammoniac, by the odour of ammonia which it gives out when rubbed with lime.

According to Berzelius, and F. D'Arcet (*Ann. de Ch. et Ph.*, lvi. 282), *anhydrous succinic acid* is composed of

				D'Arcet.	Berzelius.
Carbon	4	24	48	48.48	47.600
Hydrogen	2	2	4	3.96	4.512
Oxygen	3	24	48	47.56	47.888
<i>Anhydrous succinic acid</i>	1	50	100	100.00	100.000

And the *crystallized acid* includes an atom of water; so that the equivalent of the *anhydrous succinic acid* is 50, and that of the *hydrous or crystallized*, 59. The symbol of the former being ($4\text{ car} + 2\text{ h} + 3\text{ o}$) or *SUC'*; and that of the latter ($4\text{ car} + 3\text{ h} + 4\text{ o}$) or *SUC' + q*.

SUCCINATES.—In the *neutral succinates*, as in the benzoates, the oxygen in the acid is to that in the base as 3 to 1. They resemble the benzoates in appearance and in solubility, but the benzoates of lime, baryta, and mercury, are more soluble than the corresponding succinates. They are decomposed by the stronger acids, and by dry distillation; in the latter case the acid is resolved into water, an oily matter, and carburetted hydrogen and carbonic oxide.

SUCCINATE OF AMMONIA forms acicular crystals, which sublime when cautiously heated. Its solution has been used as a test for iron, the peroxide of which it throws down from its neutral solutions in the form of a reddish-brown precipitate.

SUCCINATE OF POTASSA is a very soluble deliquescent salt, crystallizable with difficulty in small prisms.

SUCCINATE OF SODA forms transparent four and six-sided prisms, considerably less soluble than the preceding, and permanent in the air.

SUCCINATE OF LIME forms permanent and difficultly-soluble crystals.

SUCCINATE OF BARYTA is formed by adding succinate of ammonia to nitrate of baryta. A portion is thrown down in a pulverulent form, and a part in small crystalline grains.

SUCCINATE OF STRONTIA may be formed as the preceding, and presents similar properties. It burns with a fine red flame.

SUCCINATE OF MAGNESIA is deliquescent and uncrystallizable.

SUCCINATE OF MANGANESE has been examined by Dr. John. (GEHLEN'S *Journal*, iv.) It is crystallizable, and of a slight-red tinge.

SUCCINATE OF IRON.—The *protosuccinate* is crystallizable and soluble; the *persuccinate* is insoluble, and is thrown down in the form of a brownish-red flaky precipitate from solutions of the peroxide of iron. This salt has been proposed as a means of separating iron in analysis, but in the greater number of cases it is inconvenient.

SUCCINATE OF ZINC furnishes long slender crystals.

SUCCINATE OF TIN.—The succinic acid dissolves protoxide of tin, and forms with it thin broad transparent crystals.

SUCCINATE OF COPPER.—The neutral salt is soluble, and when digested with oxide of copper yields an insoluble *subsuccinate*.

SUCCINATE OF LEAD is thrown down in the form of an anhydrous powder ($\text{PL} + \text{SUC}'$). It is soluble in excess of the acid, and yields a crystallizable *bisuccinate*, and a *basic succinate* by the action of ammonia.

SUCCINATE OF MERCURY is very difficultly soluble.

SUCCINATE OF SILVER forms delicate lamellar crystals.

SUCCINONE.—This term has been applied to the oleaginous product of the destructive distillation of succinate of lime.

SUCCINAMIDE.—When ammonia acts upon dry succinic acid, heat is evolved, water is given off, and a fusible crystallizable *amide* is formed, soluble in alcohol and water. In its anhydrous state it consists, according to D'Arcet, of

				D'Arcet.
Carbon	8	48 48.93
Hydrogen	5	5 4.98
Oxygen	4	32 31.96
Nitrogen	1	14 14.13
Anhydrous succinamide	1		99	100.00

The crystallized succinamide includes 2 equivalents of water; so that the symbol of the *anhydrous* compound being ($8\text{ car} + 5\text{ h} + 4\text{ o} + n$), = 99: that of the *hydrated* is ($8\text{ car} + 7\text{ h} + 6\text{ o} + n$), = 117.

CAOUTCHOUC.—I place this curious vegetable product among the resins, though it more strictly belongs to the modifications of *hydrocarbon*, for, according to Faraday's analysis, it consists, when deprived of adhering impurities, of carbon and hydrogen only. It is obtained from the sap of several South American and Oriental plants, more especially from the *Hevea caoutchouc*, the *Iatropa elastica*, the *Ficus Indica* and the *Artocarpus integrifolia*. It first exudes in the form of a milky juice, from which the caoutchouc gradually separates. (For some experiments on the relation between the temperature and elasticity of caoutchouc, see THOMSON'S *Organic Chemistry*, p. 696.) It is insoluble in water and in alcohol, but dissolves sparingly in washed ether. Some of the liquid hydrocarbons soften and dissolve it in a very remarkable manner, and yield compounds which have been importantly applied to the manufacture of water-proof clothing. It is also said to be similarly soluble in oil of turpentine, which perhaps may be the case when that oil has been reduced to the state of a pure hydrocarbon; but common oil of turpentine always leaves the caoutchouc more or less altered and viscid, on evaporation: the same is the case with the generality of the volatile oils. It is only difficultly acted upon by acids and alkalis. It burns in the air with a bright smoky flame: when heated, it fuses, and remains more or less viscid: subjected to destructive distillation, it yields a large relative proportion (about 83 per cent.) of a highly volatile and inflammable liquid hydrocarbon, which has been called *caoutchoucisin*, the specific gravity of which is only 0.64. This product, which is applicable to many useful purposes in the arts, is made upon a large scale by Messrs. Enderby of London: it is a solvent of caoutchouc itself, and of other substances used as varnishes. The various applications of caoutchouc in the manufacture of elastic articles and other useful products, are as yet probably in their infancy only: the consumption of it for water-proof and air-tight textures, is already very considerable. It would appear from Thomson's reference to Dalton's

experiments, that the elements of caoutchoucisin are 85.7 carbon, 14.3 hydrogen, and that the specific gravity of its vapour is 1.94: it is therefore analogous to 2 volumes of olefiant gas condensed into 1, or ($4\text{ car} + 4\text{ h}$), which is the constitution of etherine or quadrihydrocarbon (tetartohydrocarbon of Thomson).

§ XVI. BITUMENS. COAL. TAR, &c.

BITUMENS are fossil substances, bearing considerable resemblance to oily and resinous bodies, from which, and from coal, they have probably been produced by the action of subterranean fire. The chemical habitudes of several of these substances have been investigated by Mr. Hatchett (*Phil. Trans.*, 1804); and more lately by Reichenbach, Laurent, Regnault, Boussingault, and others. The following are the principal varieties:—

a. NAPHTHA has already been described as a binary compound of carbon and hydrogen (p. 550).

b. PETROLEUM has most of the properties of naphtha, but is less fluid, and darker coloured. In the countries where it abounds, it is employed for burning in lamps. By distillation, it affords a substance resembling naphtha, and mineral pitch, or asphaltum, remain in the retort.

c. MINERAL TAR appears to be petroleum further inspissated. It is more viscid, and of a deeper colour.

d. MALTHA, or MINERAL PITCH, is a soft inflammable substance, heavier than water, and may be considered as derived from the exsiccation of mineral tar.

e. ASPHALTUM is found abundantly on the shores of the Dead Sea, in Albania, and in the Island of Trinidad. Its colour is brown or black; it is heavier than water, and readily soluble in naphtha. Asphaltum was one of the materials used by the ancient Egyptians in embalming; hence termed *mumia mineralis*. At Babylon it was used for mortar. It dissolves in naphtha, and the solution forms a good varnish.

f. ELASTIC BITUMEN, or MINERAL CAOUTCHOUC, is found only in the vicinity of Castleton in Derbyshire, and at Montrelais in France. It is fusible and inflammable, and when distilled, *per se*, affords products corresponding to petroleum and asphaltum.

g. MINERAL ADIPOCIRE, or HATCHETINE, is a fatty matter found in the argillaceous iron ore of Merthyr: it is fusible at about 160° , and inodorous when cold, but of a slightly bituminous odour when heated, or after fusion. The curious products, called by Boussingault *Asphaltene* and *Petrolene* (*Ann. de Ch. et Ph.*, LXIV.), appear to belong to this class of bituminous products.

The above substances are insoluble in water, and difficultly soluble in alcohol, with the exception of naphtha and petroleum, which are soluble in highly-rectified alcohol. Some of them are hydrocarbons, and some contain small relative proportions of oxygen.

h. RETINASPHALTUM is a substance which accompanies the Bovey coal of Devonshire. I have also found it in some of the Staffordshire coal.

It was first analyzed by Mr. Hatchett, who found it to consist of 55 resin, 41 asphaltum, 4 earthy matter and loss.

i. **PIT COAL.**—There are three chemical varieties of this important substance. 1. The first, or *brown coal*, retains some remains of the vegetables from which it has originated. When heated, it exhales a bituminous odour, and burns with a clear flame. It is generally of a tough consistency, and yields, according to Mr. Hatchett, a portion of unaltered vegetable extract, and resin. 2. The second variety, or *black coal*, is the ordinary fuel of this country. It exhibits few or no traces of vegetable origin, and consists principally of bitumen and charcoal, in variable proportions. When exposed to heat it swells, softens, and burns with a bright flame, leaving a small quantity of ashes. Many varieties, however, abound in earthy matter, and these produce copious cinders, and burn with a less intense heat. The products of the destructive distillation of this kind of coal have been already described (p. 554). The residue is a hard, sonorous charcoal, termed *coke*, and containing the earthy ingredients of the coal. 3. The third variety, or *glance coal*, consists almost entirely of charcoal and earthy matter. It burns without flame, and, when distilled, yields scarcely any gaseous products. All the varieties of common coal contain nitrogen, and afford ammonia when subjected to destructive distillation. In consequence of the enormous quantities of pit coal distilled for the production of illuminating gas, a part of the commercial demand for ammoniacal salts is now supplied from that source. Dr. Thomson arranges the different kinds of British coal under the following divisions. (*Ann. of Phil.*, xiv.) 1. *Caking coal*; 2. *Splintery coal*; 3. *Cherry coal*, which is less hard and more slaty in fracture; 4. *Cannel coal*, such as that from Wigan in Lancashire. These varieties he states to be composed as follows:—

	<i>Caking coal.</i>	<i>Splint coal.</i>	<i>Cherry coal.</i>	<i>Cannel coal.</i>
Carbon	75.28	75.00	74.45	64.72
Hydrogen	4.18	6.25	12.40	21.56
Nitrogen	15.96	6.25	10.22	13.72
Oxygen	4.58	12.50	2.93	0.00
	100.00	100.00	100.00	100.00

The proportion of nitrogen here given appears enormous. Regnault, in his laborious researches on the composition of the mineral combustibles, never found more than from 1.5 to 2 per cent. (*Ann. de Ch. et Ph.*, Lxvi. 365.) Dr. Ure (*Phil. Trans.*, 1822, p. 467) obtained the following results:—

	<i>Cannel coal.</i>	<i>Splint coal.</i>
Carbon	72.22	70.90
Hydrogen	3.93	4.30
Nitrogen	2.80	0.00
Oxygen	21.05	24.80
	100.00	100.00

Dr. Henry regards Dr. Ure's results, as far as concerns the oxygen, to be the most correct, but he always obtained *ammonia* from both the above varieties of coal, and therefore infers the existence of nitrogen, though scarcely to the extent given by Dr. Thomson. The following are Dr. Thomson's results, as to the volatile products, coke and ash, in

	<i>Volatile Products.</i>	<i>Weight of Coke.</i>	<i>Incombustible Ash.</i>
1000 parts of caking coal	. . 226 . .	774 . .	15
— splint coal	. . 352 . .	647 . .	95
— cherry coal	. . 477 . .	522 . .	100
— cannel coal	. . 600 . .	400 . .	110

k. PEAT and TURF consist principally of the remains of vegetables, having undergone comparatively little change. They often contain bituminous wood, branches and trunks of trees, and vegetable extract and ulmin.

l. MELLILITE, or HONEYSTONE, is a rare substance, found in the brown coal of Thuringia, and in Switzerland. It is of a honey-yellow colour, crystallized in octoëdra, and, when analyzed by Klaproth, was found to consist of alumina combined with a peculiar acid, which has been termed *Mellitic acid*.

MELLITIC ACID is obtained by digesting the native *mellitate of alumina* in carbonate of ammonia or potassa, decomposing the resulting alkaline salt by acetate of lead, which produces an insoluble *mellitate of lead*, and which, diffused through water, and exposed to a current of sulphuretted hydrogen, yields sulphuret of lead, and the *mellitic acid* is set free. It has a peculiar sour, bitter, and sweet taste, is very soluble in water and alcohol, and crystallizes in white needles: it is not altered by nitric or hydrochloric acid, but is modified when boiled with anhydrous alcohol: it has been analyzed by Liebig and Wöhler (*Ann. de Ch. et Ph.*, xliii. 200), who consider it, in its *anhydrous* state, as an acid of carbon, composed of 4 atoms of carbon + 3 of oxygen, and containing, in its *hydrated* state, 1 atom of water. So that, in the latter state, it may be represented by $(4\text{ car} + 4\text{ o} + h)$, or $(4\text{ car} + 3\text{ o} + q)$. Its analogy to oxalic acid is obvious: its salts are less soluble than the oxalates.

TAR.—This term is applied to one of the products of the destructive distillation of organic substances, and is designated, according to its source, *vegetable tar*, *coal tar*, and *animal tar*. It is brown or black, of a thick consistency, and a strong and peculiar odour, varying with its source. It has been frequently the subject of experiment, but has lately acquired peculiar interest from the researches of Reichenbach, who has obtained from it several definite compounds, of which the most remarkable are the following:—

1. PARAFFINE.—When beech tar is distilled, three liquids pass into the recipient: 1. a light oil; 2. an aqueous acid; 3. a heavy oil. The *heavy oil* is subjected to several redistillations, and then sulphuric acid is gradually added to it, till the mixture becomes a black and thin liquid; and if it does not spontaneously rise in temperature to 212° , it is to be heated up to that point: the mixture is then kept for twelve hours, or more, at a temperature of about 122° , when a colourless oil will be found floating upon its surface, which is to be carefully poured off, and, on cooling, the *paraffine* concretes upon its surface: it is to be removed, washed, and pressed in folds of bibulous paper, and finally purified by solution in hot anhydrous alcohol, from which it separates, on cooling, in a solid form; it is somewhat flexible, and not greasy; crystalline, tasteless, and odourless: at 112° it fuses into a transparent oily liquid, and at

a higher temperature boils and distils without change: its vapour burns with a white sootless flame. Its specific gravity is 0·870. Its name is derived from its inertness as a chemical agent, or its want of affinity (*parum affinis*). It resists the action of acids, alkalis, chlorine, and potassium, and cannot be united by fusion with camphor, naphthaline, benzoin, or pitch; but it unites with stearine, cetine, bees'-wax, colophony, and readily dissolves in oil of turpentine and in naphtha. 100 parts of ether dissolve 140 of paraffine at the temperature of 75°; at a lower temperature the solution concretes into a white crystalline mass. It separates from its hot alcoholic solution in crystalline laminae, when not too concentrated. According to J. Gay Lussac (*Ann. de Ch. et Ph.*, L. 78), it is a binary compound of carbon and hydrogen, and its elements are in the same ratio as those of olefiant gas, &c., but as the density of its vapour has not been determined, its atomic constitution, and its equivalent, remain unascertained. Paraffine appears to exist in the fossil wax of Moldavia (MAGNUS, *Ann. de Ch. et Ph.*, LV. 217), and in the product of the distillation of bituminous schist. (LAURENT, *Ibid.*, LIV. 392.)

EUPION.—This liquid was also discovered by Reichenbach. (*Ann. de Ch. et Ph.*, L. 69.) It is associated with paraffine; but it is most abundant in *animal tar*, especially that obtained from horn or bones. This tar is distilled, so as to yield about three-eighths: this last product is mixed with an eighth of sulphuric acid, and the lighter yellow liquid which then separates is poured off, mixed with its weight of sulphuric acid, and distilled; a colourless liquid passes over, which is to be mixed with a solution of potassa; after some time it separates upon the surface of the mixture, when it is to be poured off, mixed with a fourth its weight of sulphuric acid, and again distilled, washed with hot solution of potassa, decanted off as before, and slowly distilled with water till three-fourths have passed over: this ultimate product is placed in vacuo for 24 hours, then heated to its boiling-point with a few grains of potassium, and when it no longer is at all acted on by that metal, it is allowed to cool and poured from the deposits: it is then *eupion*. If it contain paraffine, the two may be separated by distillation with water, and the first portions which pass over are then entirely free from it.

Eupion is tasteless, colourless, inodorous, very limpid, specific gravity 0·74; it remains liquid at -4°, and boils at about 340°, distilling over without change. It is a non-conductor of electricity. Its vapour burns with a pure white flame. It is insoluble in water. 100 parts of alcohol at 66°, dissolve 33 parts, but at a lower temperature the greater part of the eupion separates. Acetic ether dissolves about a third of eupion; sulphuret of carbon, oil of turpentine, naphtha, and almond and olive oil readily mix with it: it dissolves chlorine and bromine, and again evolves them when heated: with iodine it forms a blue solution: aided by heat it dissolves phosphorus, sulphur, and selenium, but deposits the greater portion on cooling. It dissolves naphthalin, camphor, stearin, cetine, cholesterine, and paraffine, at common temperatures, and more abundantly when heated. Caoutchouc swells in it, and dissolves when heated, but the solution remains glutinous when spread upon a surface, except it be dried by heat. The acids and alkalis are without action on eupion, and

it is not altered by exposure to air. It has not been analyzed. Its name is derived from *ευ, well*, and *πικρον, greasy*, for it has the greasiness of a fixed oil.

KREOSOTE, OR CREOSOTE (from *κρεας, flesh*, and *σωζω, I save*).—This interesting product was discovered also by Reichenbach. (*Ann. de Ch. et Ph.*, liii. 325.) It is obtained from *wood tar*, which is subjected to distillation till the residue has the consistency of pitch; but the process should not be urged too far. Oil, and acid water pass over; the former is separated, and distilled in a glass retort (not to dryness), when two products are again obtained, of which the acid water is rejected as before, and the oil preserved. In these distillations, the oil which first passes over is lighter than that which succeeds, its density augmenting with the heat: the lighter oil contains but little kreosote, and consists chiefly of eupion and lighter products: the *heavy* portion is pale-yellow, but becomes brown by exposure to air; it has a disagreeable odour, and tastes caustic, sour, sweet, and bitter. To this heavy oil, carbonate of potassa is added as long as it effervesces; it is then poured off from the produced acetate of potassa, and redistilled (not to dryness): the lighter part is again rejected, and the heavy oil is now dissolved in a solution of caustic potassa of the specific gravity 1.12; heat is evolved, and an insoluble compound of eupion, and other oils, floats upon the surface and is removed. The alkaline solution is then gradually heated in an open capsule to its boiling-point; it rapidly absorbs oxygen, and becomes brown; it is suffered to cool in the air, and then dilute sulphuric acid is added, which causes the oil to separate. This oil is now mixed with water and a little caustic potassa, in a retort, and the mixture subjected to rapid ebullition; but in consequence of the feeble tension of kreosote vapour at 212° , it passes slowly over; at length a period arrives when, although much oil remains in the retort, but little passes over, notwithstanding the heat is raised: it is then time to stop the process; the residue contains *picamar*, sulphate and acetate of potassa, and a brown substance.

The oil in the receiver is now separated from the water, and again dissolved in a similar solution of potassa: a portion of light insoluble oil separates as before, which, being removed, the mixture is again heated in an open vessel, and as it slowly cools it again becomes brown, but less so than formerly; sulphuric acid is then added in slight excess, and the evolved oil is washed, as long as it is acid, with cold water. The distillation of this oil with water is again repeated, but, instead of adding potassa, a little phosphoric acid is employed to abstract a portion of ammonia which the oil still retains. The distilled oil is now, for the third time, dissolved in the caustic potassa, and if the precautions above described have been attended to, they combine without the separation of any oily matter, and the mixture, exposed to air, only acquires a slight red tinge. When the kreosote is now ultimately separated from its combination with the potassa, it is sufficiently pure for medical use: to obtain it absolutely pure, it must be distilled with water, and this hydrated product again rectified; water first goes over, and afterwards, at a high temperature (203° Cent.), the kreosote: to deprive it absolutely of water, its vapour must be passed over chloride of calcium.

I have taken the above details from Dumas: the process, though not difficult, is, as he observes, very troublesome, but methods of improving and facilitating it will doubtless be discovered.

Kreosote, when pure, is a colourless transparent liquid, of great refractive power, a penetrating and strong odour resembling that of smoked meat: it has a burning caustic taste: its specific gravity is 1.037 at 65°; it boils at 397° (203° Cent.), and retains its fluidity at -17°. It is a non-conductor of electricity, and it burns with a very sooty flame. When mixed with water, two solutions result; the one consisting of 1.25 kreosote + 100 water; the other, of 100 kreosote + 10 water. The aqueous solution is neither acid nor alkaline.

Pure kreosote dissolves oxide of copper, forming a brown solution: when boiled with peroxide of mercury, it is reduced, and the kreosote converted into a resin. It produces effervescence and red fumes with nitric acid: it absorbs chlorine, and is gradually changed by it into a resin. It is coloured by bromine, iodine, sulphur, and phosphorus. With potassium it evolves gas, and potassa is formed, which combines with the kreosote. It is thickened and blackened by concentrated sulphuric acid. Acetic acid is its most perfect solvent. It forms two compounds with potassa; the one anhydrous, liquid, and of an oily consistence; the other hydrated, and crystallizable in nacreous plates. All the acids decompose these compounds, and separate unaltered kreosote. With soda it produces similar combinations. It also combines with ammonia, lime, and baryta. It dissolves many salts. Alcohol, ether, sulphuret of carbon, eupion, naphtha, and acetic ether, dissolve it in all proportions. It does not combine with pure paraffine. It dissolves the resins, and all colouring matters, including those of cochineal, saunders-wood, dragons'-blood, madder, saffron, and, with the aid of heat, indigo. Its action upon caoutchouc, unlike that of eupion, is very feeble.

Kreosote immediately coagulates egg-albumen, although much diluted; it also coagulates serum. Meat and fish are preserved after having been brushed over with kreosote and dried in the sun; and it appears to be the principle to which the antiseptic powers of wood-smoke, and pyroligneous acid are due. Its action upon the animal system is energetic; it is painful upon the tongue, destroys the epidermis, and kills fishes and insects: it also destroys vegetation. It is medicinally employed in tooth-ach, cancer, ulcers, and cutaneous diseases, externally; and to check hæmorrhage; and internally as a stimulant, and for the prevention of nausea and vomiting. Three or four drops, added to a pint of ink, effectually prevent its mouldiness. According to Ettling, (*Ann. de Ch. et Ph.*, Liii. 333,) it consists of 77.42 carbon, 8.12 hydrogen, 14.46 oxygen; but, as it probably retains a variable portion of water, its atomic constitution cannot be accurately inferred.

PICAMAR.—This is the bitter principle of tar; whence it derives its name (*Picis amarum*). It is contained in the heavy oil of wood tar; that portion, the specific gravity of which exceeds 1.095, is mixed with 8 parts of a solution of potassa, specific gravity 1.15, and left to itself: a layer of impure eupion and paraffine separates upon the surface, after which the liquor clears, and in 24 hours deposits brilliant acicular or

lamellar crystals; these are dried between folds of blotting paper, and repeatedly dissolved in boiling solution of potassa, till the mother liquors are colourless, and the crystals buff-coloured: they are then decomposed by dilute phosphoric acid, which combines with the potassa, and separates a brownish limpid oil, which, after having been two or three times redistilled with water acidulated by phosphoric acid, is ultimately carefully rectified without addition. The product thus obtained is *picamar*. It is almost colourless and transparent; its consistency is that of oil, and it is greasy. It is insupportably bitter, with an aroma like peppermint; its specific gravity is 1.10 at 65°. It boils at 545°, being less volatile than kreosote. Nitric and hot sulphuric acid decompose it: it dissolves in acetic acid, and is the source of the bitter flavour of crude pyroligneous acid. It is soluble in all proportions in alcohol, and in sulphuric and acetic ether, and in kreosote. It neither dissolves paraffine, asphaltum, nor amber: it takes up caoutchouc when hot, but deposits it again on cooling. It forms crystallizable compounds with potassa, which are almost insoluble in pure alcohol: weak alcohol dissolves the crystals when hot, but deposits them again as it cools. When impure, these crystals gradually become brown or blue. It also combines with ammonia, soda, lime, and baryta, but the bases are not neutralized in any of these compounds. Picamar reduces red oxide of mercury to the metallic state, and minium to the state of protoxide.

PITTACAL.—When a few drops of baryta-water are added to an alcoholic solution of impure picamar, or even of oil of tar, deprived of its acid, the liquor immediately assumes a bright blue tint, which in a few minutes passes into an indigo colour. Dumas considers this substance identical with a blue product obtained, in 1827, from coal tar, by MM. Barthe and Laurent. Reichenbach gave it the above name, from *πιττα*, *pitch*, and *καλλος*, *ornament*.

The mode of separating pittacal has not been clearly described: Dumas states, that when precipitated in a flocculent state from its solutions, or obtained by evaporation, it closely resembles indigo, and, like it, acquires a coppery hue when rubbed: it is inodorous, tasteless, and not volatile: at a high temperature it becomes charred without evolving ammonia. It is decomposed by nitric acid; hydrochloric and dilute sulphuric acid dissolve it; and it is abundantly soluble in acetic acid, forming a red liquid, which, when saturated by an alkali, becomes of a bright blue. Reichenbach represents it as a more delicate test of acids and alkalis than litmus. It is insoluble in alcohol, in ether, and in eupion. With acetate of lead, protochloride of tin, ammonio-sulphate of copper, and acetate of alumina, it yields a fine blue colour with a tint of violet: these combinations may probably be useful as dye-stuffs, for they are not affected by air or light. It is said, like indigo, to contain nitrogen, but its ultimate composition has not been accurately determined.

CAPNOMOR, (*καπνος*, *smoke*, and *μοιρα*, *part*, because it forms part of wood smoke.)—This is a colourless transparent liquid of a pungent and rather agreeable odour, which occurs with the above products in the heavy oil of tar. When that oil is digested with solution of potassa, the kreosote, picamar, and pittacal, are taken up, and *capnomor*, with a little

eupion, floats upon the surface: this is separated and mixed with sulphuric acid, which dissolves the capnomor and leaves eupion; carbonate of potassa separates the capnomor from its acid combination, and it is purified by distillation. Its specific gravity is 0.975: it boils at 365°. It is insoluble in water and the alkalis, but soluble in alcohol, in ether, and in eupion. Its composition has not been determined.

The above is an outline of the history of the extraordinary products contained in tar: when considered in reference to the various hydrocarbons already noticed, as producible from coal-tar, and by the destructive distillation of resins and oils, the whole subject acquires a considerable degree of interest, and leaves little doubt that the apparent complexity and incongruity which hangs over the inquiries as they now stand, will be done away by the further examination of their mutual relations, and by the attainment of more exact views of their ultimate and atomic constitution.

§ XVII. VEGETABLE ACIDS.

THIS section will be devoted to the *tartaric*, *oxalic*, *citric*, and *malic acids*, which are the principal of those found ready formed in our common fruits, and are of important application in the arts and domestic economy, and to a few other acids of more rare occurrence, or which, by analogy, may be ranked with the above. The general constitution of these acids has been elsewhere noticed, and their individual analyses are given in this section and elsewhere; they have recently engaged the attention of several celebrated analysts, more especially of Liebig and Dumas. An elaborate essay by the former will be found in the *Ann. de Ch. et Ph.* (LXVIII. 5.)

1. TARTARIC ACID.—Scheele first obtained crystallized tartaric acid in the year 1770. It exists *free* in the pulp of tamarinds, in grapes, and in the pepper plant; as *tartar*, in tamarinds, grapes, mulberries, and samphire; in the root of wheat (*Triticum repens*), and of dandelion (*Leontodon taraxacum*), in the berries of sumach (*Rhus coriaria*), and in the rhubarb plant, the potato, madder, and Iceland moss; as *tartrate of lime* in squills, madder root, quassia wood, the fruit of *Rhus typhinum*, and the tubercles of the *Helianthus tuberosus*. (GMELIN.)

Tartaric acid is generally obtained from the *bitartrate of potassa*. Mix 100 parts of this salt in fine powder with 30 of powdered chalk, and gradually throw the mixture into 10 times its weight of boiling water; when the liquor has cooled, pour the whole upon a little strainer, and wash the white powder which remains with cold water; this is a *tartrate of lime*; diffuse it through a sufficient quantity of water, add sulphuric acid equal in weight to the chalk employed, and occasionally stir the mixture during 24 hours; then filter, and carefully evaporate the liquor to about one-fourth its original bulk; filter again, and evaporate with much care nearly to dryness; redissolve the dry mass in about 6 times its weight of water, render it clear by filtration, evaporate slowly to the consistency of syrup, and set aside in a warm place to crystallize. By two or three successive solutions and crystallizations, tartaric acid will be

obtained in nearly colourless crystals; they may be perfectly whitened by the aid of a little animal charcoal. Tartaric acid may also be obtained by neutralizing 1 part of tartar by carbonate of potassa, and digesting the solution for an hour with 8 parts of quicklime, decanting the liquor (which contains caustic potassa), washing the residue with dilute acetic or hydrochloric acid to free it from excess of lime, and then decomposing it by dilute sulphuric, as above. (OSANN.) Dr. Henry states, that in this process the free potassa prevents the precipitation of the tartrate of lime. Fabroni obtained tartaric acid by adding excess of powdered tartar to a boiling mixture of 1 part of sulphuric acid and 3 of water; the solution, on cooling, deposits some tartar and sulphate of lime, from which it is poured off and evaporated to a small bulk; alcohol is then added, which dissolves out the tartaric acid, and leaves bisulphate of potassa. (*Ann. de Ch. et Ph.*, xxv. 9.) Tartaric acid may also be obtained by decomposing tartrate of lead, diffused through water, by sulphuretted hydrogen.

Crystallized tartaric acid is intensely sour: its specific gravity is 1.6; it is generally semitransparent, and of complicated forms which appear to be modifications of a rhombic prism. (BROOKE, *Ann. of Phil.*, 2nd series, vi. 118. PECKET, *Ann. de Ch. et Ph.*, xxxi. 78.) It is not altered in a dry atmosphere, but in humid air it tends to deliquescence. At a little above 212° it melts into a transparent liquid, boils at 250° , and, on cooling, concretes into a granular mass, which is more deliquescent than the original acid. If the heat be continued, it becomes yellow, exhales a peculiar odour, and begins to be decomposed. Water dissolves 1.5 its weight of tartaric acid at 60° , and twice its weight at 212° . The concentrated solution has the consistence of syrup. The solubility of this acid is, however, variously stated, and it is not easy, under common circumstances, to dissolve more than 1 part of the crystals in 4 or 5 water; but when a boiling solution is cooled to 60° , it retains much more. It is also soluble in alcohol. The aqueous solution of tartaric acid soon becomes mouldy, and suffers decomposition. Boiled in nitric acid, tartaric acid is partly converted into oxalic acid; and sulphuric acid converts it into acetic. It becomes converted into oxalic acid by fusion with potassa.

When tartaric acid is submitted to destructive distillation, it affords a brown acid liquor, containing an oily matter, acetic acid, pyroacetic spirit, and pyrotartaric acid. If this liquor, after having been passed through a wet filter to separate the oil, be saturated with carbonate of potassa, and evaporated to dryness, a saline mass is obtained, which, after having been twice or thrice redissolved and crystallized, is rendered free from foreign matter. If this salt be distilled with sulphuric acid, diluted with its weight of water, an acid liquor passes over, succeeded by a white sublimate of pure pyrotartaric acid. Rose, who has examined the properties and combinations of this body, considers it as a distinct acid; the pyrotartrates of ammonia, potassa, soda, baryta, strontia, and lime, are very soluble. The pyrotartaric acid occasions precipitates in acetate of lead, and in nitrate of mercury, and is thus, according to Rose, distinguished from tartaric acid, which only throws down the former;—but this is not a correct distinction. The action of heat upon tartaric acid has been studied by M. E. Fremy (*Ann. de Ch. et Ph.*, lxxviii. 353); he

describes several modifications of the acid (under the names *tartralic* and *tartrelic* acids) depending upon the relative proportion of water combined with the anhydrous acid. It also appears, from the experiments of Pelouze (*Jour. de Pharm.*, xiii. 61), that another acid is produced during the production of the pyrotartaric acid, which he has called *pyruvic acid*.

Tartaric acid is distinguished by the white granular precipitate which it produces when added in excess to solutions containing potassa. It produces a white precipitate, soluble in excess of acid, in lime, baryta, and strontia-water, and in acetate of lead. It is used in calico-printing, and is much employed as a cheap substitute for citric acid in lemonade and effervescent solutions: in the laboratory it is used as a test of the salts of potassa, and to prevent the precipitation of certain oxides, as that of antimony, and the titanio acid.

Tartaric acid, as it exists in *anhydrous* combination with bases, may be represented by the equivalent 66, (66 THOMSON, 66 GMELIN, 66·48 TURNER,) and its hypothetical composition in reference to this atomic weight will be ($4\text{ car} + 2\text{ h} + 5\text{ o}$), or

						Berzelius.		
Carbon	.	4	.	24	.	36·36	.	35·980
Hydrogen	.	2	.	2	.	3·03	.	3·807
Oxygen	.	5	.	40	.	60·61	.	60·213
<hr/>						<hr/>		
Tartaric acid	1			66		100·00		100·000

The *crystallized* acid is constituted of

				Berzelius.
Anhydrous tartaric acid	1	. . .	66 . . . 88 . . .	88·06
Water	1	. . .	9 . . . 12 . . .	11·94
<hr/>				<hr/>
Crystallized tartaric acid	1		75 . . . 100 . . .	100·00

TARTRATE OF AMMONIA ($\text{tar}' + \text{A}$) forms very soluble prismatic crystals, of a cooling taste. The addition of tartaric acid to its aqueous solution, produces a precipitate of a difficultly-soluble *bitartrate* of ammonia. When a saturated solution of tartaric acid is added to strong liquid ammonia in such proportions as to form the bitartrate, the liquids solidify with great rise of temperature.

TARTRATE OF POTASSA ($\text{tar}' + \text{P}$) is formed by saturating the excess of acid in *tartar*, by potassa. The resulting salt is soluble in less than twice its weight of water, (hence, in opposition to the bitartrate, termed *soluble tartar*.) It crystallizes in four and six-sided prisms with diëdral summits, but its primitive form is a right rhomboidal prism. (BROOKE, *Ann. of Phil.*, N. S., vii. 161.) Its taste is saline and bitter, and it is used in medicine, (formerly under the name of *Tartarus tartarisatus*,) as an aperient. It is slightly deliquescent, and almost insoluble in absolute alcohol. Most acids occasion a precipitate of bitartrate of potassa when added to the aqueous solution of this salt. Tartrate of potassa is anhydrous, and consists of

										Thomson.	Berzelius.
Potassa	1	.	48	.	42·1	.	42	.	41·31		
Tartaric acid . .	1	.	66	.	57·9	.	58	.	58·69		
<hr/>										<hr/>	<hr/>
Tartrate of potassa	1		114		100·0		100		100·00		

BITARTRATE OF POTASSA. SUPERTARTRATE OF POTASSA. TARTAR. (*2 tar' + P.*)—This substance exists in considerable abundance in the juice of the grape, and is deposited in wine casks in the form of a crystallized incrustation, called *argol*, or *crude tartar*. It is purified by solution and crystallization, which renders it perfectly white: when in fine powder, it is termed *cream of tartar*. The purification of *tartar* at Montpellier is performed as follows:—It is first dissolved in boiling water, and crystallized; these crystals are then boiled with one-twentieth their weight of pipe-clay, (and the same quantity of animal charcoal?) which absorbs the colouring matter, and falls as an insoluble sediment, the crystals of pure tartar separating afterwards upon the surface of the liquor, and upon the sides and bottom of the boiler; the term *cream of tartar* was originally applied to the imperfectly crystallized superficial crust. The details of this process are described by M. Fizes, (*Mémoires de l'Académie*, 1725,) and it is still carried on upon the same plan. The Venetian process for the purification of tartar consists in the separation of the grosser impurities by one or two preliminary solutions and crystallizations, after which, white of egg and wood ash are added to the boiling solution of the crystals, and the impurities skimmed off during the effervescence which ensues. (DESMARET, *Jour. de Phys.*, i. 67.)

Bitartrate of potassa may be formed artificially by adding excess of tartaric acid to a solution of potassa. The mixture presently deposits crystalline grains, and furnishes a striking example of the diminution of solubility by increase of acid in the salt. Upon this circumstance, the use of tartaric acid as a *test* for potassa depends, for soda forms an easily soluble supertartrate, and consequently affords no precipitate.

Its crystals, which are irregular six-sided prisms, terminated by hexaëdral summits, or triangular prisms with diëdral summits, have been described by Dr. Wollaston, (*Thomson's Annals*, x. 37,) and by Mr. Brooke, (*Ann. of Phil.*, N. S., vii. 161.) They include 1 proportional of water, which is not separable at a heat much below that at which the acid of the salt begins to be decomposed. They are hard, and taste gritty and subacid.

The specific gravity of this salt is 1.95. It requires 95 parts of water at 60°, and 15 parts at 212° for its solution. It is rendered much more soluble by the addition of boracic acid or of borax, as was first observed by Le Fevre. (*Mém.*, Paris, 1732.) 2 parts of borax, and 5 of crystals of tartar in powder, are soluble in about 6 times their weight of boiling water; on evaporating the solution to the consistency of honey, the residue concretes into *Le Fevre's soluble cream of tartar*, or *sal-gummosum*. It is the *tartarus boraxatus* of some old writers. When exposed to heat, tartar fuses, blackens, and is decomposed, and carbonate of potassa is the remaining result. Provided the tartar be free from lime, which however is seldom the case, this furnishes a good process for obtaining pure *carbonate* of potassa. By destructive distillation, Fourcroy and Vauquelin obtained the following residuary substances from 1000 grains of crystals of tartar. (*Ann. de Chim.*, Lxiv. 43.)

Carbonate of potassa . . .	350	Alumina	0.25
Carbonate of lime . . .	6	Iron and manganese . . .	0.75
Silica	1.2		

The aqueous solution of tartar becomes mouldy when exposed to air, and the tartaric acid being entirely decomposed leaves a weak solution of carbonate of potassa. Tartar sometimes acts as a simple acid, and dissolves oxides insoluble in most other acids; hence Gay Lussac has suggested its use in certain analyses. (*Ann. de Ch. et Ph.*, iii. 281.) By the action of excess of caustic potassa, at high temperatures, tartar is converted into oxalate of potassa. The component parts of tartar render it an excellent flux in the reduction of metallic ores upon a small scale, its alkali promoting their fusion, and the carbonaceous matter tending to reduce the oxides. Tartar is sometimes adulterated by the addition of pounded quartz, and by calcareous spar; the former may be detected as an insoluble residue by boiling the powdered tartar with half its weight of carbonate of potassa or of borax in 8 parts of water; the latter produces effervescence with dilute hydrochloric acid. A small portion of tartrate of lime is almost always present in the purified tartar; it separates in tufts of acicular crystals from the hot solution of the tartar.

TARTRATE OF POTASSA AND AMMONIA is formed by saturating the excess of acid in tartar with ammonia. It forms transparent four and six sided prisms, very soluble in water, and which effloresce and lose ammonia by exposure to air.

TARTRATE OF SODA (*tar'* + S) forms acicular crystals, soluble in about their own weight of water, and insoluble in absolute alcohol. They contain, according to Bucholz, 16 per cent. (2 equivalents) of water. When their aqueous solution is mixed with half their weight of tartaric acid, it yields small prismatic crystals of *bitartrate of soda*, of an acid taste, soluble in 8 parts of cold and 1.8 of boiling water, and containing about 15 per cent. (3 equivalents) of water of crystallization. (GEHLEN'S *Journ.*, v. 520.) Tartrate of soda is often formed extemporaneously by dissolving equal parts of powdered tartaric acid and of bicarbonate of soda, in separate portions of water, and then mixing the solutions; if taken during the effervescence, it forms a refreshing saline and slightly aperient draught.

TARTRATE OF POTASSA AND SODA (2 *tar'* + P + S) is prepared by saturating the excess of acid in tartar, with carbonate of soda; it is the *soda tartarizata* of the *Pharmacopœia*; it forms prismatic crystals, which have been described by Mr. Brooke. (*Ann. of Phil.*, N. S., v. 451.) It has long been used in Pharmacy under the name of *Rochelle Salt* and *Sel de Seignette*. The crystals are soluble in about 5 parts of cold water, and consist of

				Schulze.	Vauquelin.
Potassa	1	48	15.9	14.3 Tartrate	} 54
Soda	1	32	10.6	13.3 of potassa	
Tartaric acid	2	132	43.7	41.3 Tartrate	} 46
Water	10	90	29.8	31.1 of soda	
	1	302	100.0	100.0	100

TARTRATE OF LITHIA is easily soluble; when its solution is evaporated it affords a white uncrystallized mass, opaque and not deliquescent.

Excess of tartaric acid does not give a crystallizable bitartrate. *Tartrate of Potassa and Lithia*, formed by saturating tartar with carbonate of lithia, affords quadrangular prismatic crystals, easily soluble, and very slightly efflorescent. *Tartrate of Soda and Lithia* forms rectangular four-sided prisms, easily soluble, slightly efflorescent, and of a pure saline flavour. (C. GMELIN.)

TARTRATE OF LIME (*tar'* + C) is nearly insoluble in cold water, but soluble in 600 parts of boiling water; it is produced by adding chalk to tartar, as in the process for obtaining tartaric acid, where it is decomposed by sulphuric acid. It dissolves sparingly in excess of tartaric acid, and may be obtained from such solution in small silky crystals. It is often contained in rough and purified tartar, and forms tufts of acicular crystals when tartar is saturated by bases. Dilute hydrochloric acid dissolves and decomposes it: if this solution is saturated by ammonia, the tartrate of lime is reproduced, and crystallizes after some hours in acute octoëdra. Solution of potassa dissolves tartrate of lime, and when concentrated by evaporation becomes gelatinous, but liquifies on cooling. (DUMAS.) Tartrate of lime, after desiccation at 212° , consists of

				Berzelius.	Gay Lussac and Thenard.
Lime	1	28	21.54	21.64	22.423
Tartaric acid .	1	66	50.77	50.55 }	77.577
Water	4	36	27.69	27.81 }	
<hr/>					
Tartrate of lime	1	130	100.00	100.00	100.000

TARTRATE OF POTASSA AND LIME may be formed by adding lime-water to solution of bitartrate of potassa, till it begins to become turbid: in a few days acicular crystals of the triple salt are deposited, which effloresce when exposed to air?

TARTRATE OF BARYTA (*tar'* + B) is a difficultly-soluble salt. When carefully dried it is anhydrous: it is distinguished from sulphate of baryta by its solubility in hydrochloric, nitric, and acetic acids, and by its destructibility by heat.

BITARTRATE OF BARYTA forms transparent crystals, consisting of 2 proportionals of tartaric acid ($66 \times 2 = 132$, 1 of baryta = 77, and 2 of water ($9 \times 2 = 18$). (THOMSON.)

TARTRATE OF STRONTIA is thrown down, after some hours, on mixing the solutions of tartrate of potassa and nitrate of strontia. It dissolves in rather more than 300 parts of boiling water, and forms small rhomboidal crystals as the solution cools. (VAUQUELIN.) It consists of 1 atom of tartaric acid, 1 of strontia, and 3 of water. (THOMSON.)

TARTRATE OF MAGNESIA is precipitated from the sulphate by tartaric acid: it is soluble in excess of tartaric acid, and forms a crystallizable salt. When dried at 60° , it consists of 1 proportional of anhydrous tartrate, and 2 of water. There is also a *bitartrate of magnesia*. (THOMSON.)

TARTRATE OF MANGANESE, formed by dissolving protoxide of manganese in tartaric acid, is a soluble salt, and therefore not immediately precipitated by adding tartaric acid, or a neutral tartrate, to protochloride

or protosulphate of manganese. When hot solutions of protochloride of manganese and tartrate of potassa are mixed, small crystals are deposited on cooling, which are resolved by boiling water into a soluble super-tartrate and an insoluble basic salt. (PFAFF.) The crystals consist of ($\text{tar}' + \text{MAN} + 2\text{q}$). (THOMSON.) When the protosalts of manganese are mixed with tartar, the oxide is not thrown down by pure or carbonated alkalis. (H. ROSE.) When tartaric acid and peroxide of manganese are boiled together in water, carbonic acid is evolved, and a colourless solution of prototartrate of manganese is obtained. Formic acid is also produced during the action of the acid and oxide. (*Quarterly Journal*, xiv. 232.)

TARTRATES OF IRON.—Tartaric acid acts upon soft iron with the disengagement of hydrogen gas, and a difficultly-soluble *prototartrate* of iron, nearly white, and pulverulent, is formed. At a dull red-heat, this tartrate readily takes fire, and burns slowly away like tinder, the iron becoming peroxidized. It would probably form a valuable addition to the *Materia Medica*. (URE, *Quarterly Journal*, Oct., Dec., 1829.) When hot and strong solutions of tartaric acid and protosulphate of iron are mixed, white foliated crystals of *prototartrate of iron* are deposited on cooling: this salt requires 400 parts of cold water for solution. (DUMAS.) It has a slightly inky taste, and consists of ($\text{tar}' + \text{Fe} + 2\text{q}$). (THOMSON.)

Tartaric acid has scarcely any action upon sesqui-oxide of iron, but a *pertartrate of iron* may be obtained by mixing sesqui-sulphate of iron with tartrate of potassa, in equivalent proportions. Sulphate of potassa precipitates in a crystalline powder (the solutions being sufficiently concentrated), which may be separated from the blood-red liquid pertartrate of iron by filtration. Alcohol forms a treacly precipitate in this solution.

TARTRATE OF IRON AND POTASSA.—When 1 part of iron-filings and 4 of tartar are digested together with water, a greenish, astringent, and difficultly-soluble salt is formed: it is not decomposed by pure or carbonated alkalis, but by sulphuretted hydrogen. (THENARD.) By long exposure of the mixture of tartar and iron to air, or by mixing 1 part of soft iron-filings with 4 of tartar into a thin paste with water, and digesting for some weeks, till the acid is neutralized, fresh portions of water being occasionally added to prevent exsiccation, a dark-brown uncrystallizable compound is obtained, the solution of which has been used in medicine. It is not decomposed by the alkalis. The pertartrate of iron and potassa is best obtained by digesting recently-precipitated hydrated peroxide of iron with bitartrate of potassa and water. It dissolves in alcohol.

TARTRATE OF ZINC is formed by adding tartrate of potassa to sulphate of zinc, and is a very difficultly-soluble compound. When oxide of zinc is dissolved with tartar the solution is not affected by the alkalis, but their sulphurets throw down the whole of the zinc.

TARTRATE OF TIN.—Tartrate of potassa occasions a white precipitate in the neutral protohydrochlorate and perhydrochlorate of tin. *Tartrate of potassa and tin*, formed by boiling the oxide in solution of tartar, is

very soluble; the addition of alkalis and their carbonates occasions no precipitates. (THENARD, *Ann. de Chim.*, xxxviii.)

TARTRATE OF COPPER is produced by adding tartaric acid to sulphate of copper. It forms a bluish-green crystallized precipitate. When tartaric acid is added to a solution of the neutral tartrate, a more difficultly soluble *bitartrate* falls.

TARTRATE OF POTASSA AND COPPER is formed by boiling hydrated oxide of copper and tartar in water; the solution yields blue crystals on evaporation; or if boiled to dryness, furnishes one of the pigments called *Brunswick-green*.

TARTRATE OF LEAD (*tar'* + PL) is thrown down in the form of an almost insoluble white crystalline powder, on adding tartaric acid to solution of nitrate or acetate of lead: it is soluble in excess of carbonic acid. When this tartrate is heated to a dull-red in a glass tube, it acquires a brown colour; and, when cool, forms, as was first remarked by Dr. Gobel, a very perfect *pyrophorus*, which immediately inflames on being shaken out into the air. This property appears to depend upon the rapid oxidizement of the minutely-divided metallic lead; or, perhaps, a very oxidizable carburet lead may be formed. Tartrate of lead is composed of

				Berzelius.	Thomson.	Bucholz.
Oxide of lead .	1	112	62.92	62.5	62.56	63
Tartaric acid .	1	66	37.08	37.5	37.44	37
<hr/>						
Tartrate of lead	1	178	100.00	100.0	100.00	100

TARTRATE OF POTASSA AND LEAD is formed, according to Thenard, by boiling a mixture of tartar and oxide of lead in water. (*Ann. de Ch.*, xxxviii.) It is an insoluble white powder, not decomposed by the alkalis or by dilute sulphuric acid.

TARTRATE OF ANTIMONY.—Protoxide of antimony dissolved in tartaric acid yields a very soluble, deliquescent, and difficultly-crystallizable salt.

TARTRATE OF ANTIMONY AND POTASSA. EMETIC TARTAR.—This compound may be obtained by boiling protoxide of antimony, obtained by any of the processes formerly described, with pure bitartrate of potassa. Emetic tartar is usually prepared by boiling a solution of 100 parts of tartar with 100 parts of *finely levigated* glass of antimony (or other *protoxide*); the ebullition should be continued for half an hour, and the filtered liquor evaporated to about half its bulk, and set aside to crystallize; octoëdral crystals (BROOKE, *Ann. of Phil.*, N. S., vi. 40) of the emetic salt are thus obtained; and there is generally formed along with them a portion of tartrate of lime and potassa, which is deposited in small radiated tufts, easily separated when the mass is dried.

Emetic tartar is a white salt, slightly efflorescent, soluble in about 14 parts of cold, and 2 parts of boiling water. Its solution is rendered turbid by hydrochloric, nitric, and sulphuric acids, but not by the fixed alkalis: the fixed alkaline carbonates and lime-water decompose it. Infusion of galls and many other vegetable bitter and astringent infusions form a pre-

precipitate in solution of emetic tartar, which is generally said to be inactive, and hence decoction of bark has been recommended as an antidote to its effects. Solution of sulphuretted hydrogen only precipitates very strong solutions of emetic tartar; weaker solutions are merely reddened by it. It is decomposed by hydrosulphuret of ammonia: among the metals, iron only throws down the whole of its antimony. At 212° the crystals lose about 2 per cent. of water; at a higher temperature about 7 or 8 per cent. Heated to redness, out of the contact of air, it furnishes a highly-pyrophoric residue. This salt (crystallized) consists of

				Wallquist.	R. Phillips.
Protoxide of antimony	2	154	42.6	42.99	43.35
Potassa	1	48	13.3	13.26	49.25
Tartaric acid	2	132	36.6	38.61	
Water	3	27	7.5	5.14	7.40
	1	361	100.0	100.00	100.00

TARTRATE OF BISMUTH has not been examined, but moist oxide of bismuth, boiled with tartar, forms a difficultly-soluble triple salt.

TARTRATE OF COBALT.—Tartrate of potassa forms no precipitate in solutions of cobalt, but their colour is much heightened by it. Moist oxide of cobalt is soluble in tartaric acid, and the solution furnishes red crystals on evaporation.

TARTRATE OF URANIUM is a very soluble salt, not easily crystallizable.

TARTRATE OF TITANIUM appears to be a soluble compound.

TARTRATE OF CERIUM, according to Hisinger and Berzelius, is formed by adding tartrate of potassa to sulphate, nitrate, or hydrochlorate of cerium. It is a soft, tasteless powder, soluble in nitric, hydrochloric, and sulphuric acids, and in the alkalis.

TARTRATE OF NICKEL, formed by digesting moist oxide of nickel in tartaric acid, is a very soluble salt; tartaric acid occasions no precipitate in the soluble salts of nickel.

TARTRATE OF MERCURY.—Tartaric acid occasions white precipitates in all the solutions of the oxides of mercury, not containing excess of acid.

TARTRATE OF POTASSA AND MERCURY is formed, according to Thénard, by adding solution of tartar to protonitrate of mercury; and an analogous salt of the peroxide may be obtained by boiling it in a solution of tartar.

TARTRATE OF SILVER.—Tartaric acid occasions no change in nitrate of silver, but tartrate of potassa forms a white precipitate, which is probably a tartrate of silver.

TARTRATE OF SILVER AND POTASSA is thrown down by adding tartar to nitrate of silver.

TARTRATE OF SILVER AND ANTIMONY.—The precipitate which falls on adding nitrate of silver to a solution of emetic tartar, consists of

					Wallquist.
Oxide of silver . . .	1 . .	118 . .	28.0 . .	27.31	
Protoxide of antimony	2 . .	154 . .	36.5 . .	36.94	
Tartaric acid. . . .	2 . .	132 . .	31.3 . .	31.50	
Water.	2 . .	18 . .	4.2 . .	4.25	
	I	422	100.0	100.00	

TARTRATE OF ALUMINA is a soluble uncrystallizable compound of an astringent flavour: it is not deliquescent. It exists in the *Lycopodium complanatum*, an infusion of which may be used as a mordant.

RACEMIC ACID.—A very curious modification of tartaric acid has been discovered by Mr. Kœstner, of Thann, and examined by Gay Lussac, Walchner, and Berzelius, (*Ann. de Ch. et Ph.*, xlv. 128,) who terms it *paratartaric acid*: it has been called *racemic acid*, and supposed to be peculiar to certain grapes. This acid is less soluble than tartaric acid, and its crystals instead of 1, include 2 atoms of water, one of which is given off at 212° , and the other, when it unites with bases. It is obtained by neutralizing the tartar which contains it with soda, and separating the double *tartrate* of soda and potassa by crystallization; the double *racemate* remains in the mother liquor, which, filtered through animal charcoal, and decomposed by a solution of acetate of lead, yields a mixed tartrate and *racemate of lead*; these, diffused through water and decomposed by sulphuretted hydrogen, furnish a solution of racemic and tartaric acids, from which the former may be perfectly separated by crystallization, whilst the latter remains in the mother liquor. *Anhydrous racemic acid* is represented by $(4car + 2h + 5o) = rac'$; and the *crystallized* by $(rac' + 2q)$.

II. OXALIC ACID.—This acid, which was discovered by Scheele, is found in some fruits, and in considerable quantity in the juice of the *Oxalis acetosella* or *wood sorrel*, in the *Rumex acetosa* or *common sorrel*, and in the varieties of *rhubarb*. It is occasionally found in human urine; and it occurs in the mineral kingdom in combination with oxide of iron, forming the mineral called *Humboldtite*. It is most readily procured by the action of nitric acid on certain organic substances, and especially upon sugar, and has hence been termed *acid of sugar*. It may be obtained by introducing into a retort 4 ounces of nitric acid diluted with 2 of water, and 1 ounce of white sugar; nitric oxide gas is copiously evolved, and when the sugar is dissolved, about one-third of the acid may be distilled over: the contents of the retort are then emptied into a shallow vessel, and in the course of two or three days an abundant crop of white crystals is deposited, and, upon further evaporation of the mother liquor, a second portion is obtained. The whole crystalline produce is to be redissolved in water, and again crystallized, by which the pure acid is obtained. In this way sugar yields rather more than half its weight of oxalic acid. Potato starch may be substituted for sugar in this process, 12 parts of which yield about 5 of the acid.

Oxalic acid thus procured is in the form of four-sided prisms, transparent, and of a very acid taste; their primary form is a right rhombic prism, the modifications of which have been described by

Mr. Brooke. (*Ann. of Phil.*, N. S., vi. 119.) The crystals dissolve in about 15 parts of water at 50° , and in 9 parts at 60° , their solubility increasing rapidly with the increase of temperature; at 212° , they fuse in their water of crystallization. The great solubility attributed to this acid by Bergman, seems to have depended upon the presence of nitric acid. It is less soluble in alcohol than in water. In a very dry air the crystals effloresce; at a temperature of 100° , they gradually fall into a white powder, and when thus slowly dried lose about a third of their weight. As this acid is volatile, its desiccation requires much caution: the crystals, after having been deprived of 2 equivalents of water, sublime rapidly when heated to about 330° ; the sublimate forms transparent acicular crystals, containing 1 atom of water; they absorb moisture, and become opaque by exposure to air. When the ordinary crystals are rapidly heated in a retort to about 300° , water, carbonic acid, carbonic oxide, and formic acid are the results. Passed through a red-hot tube, carbonic oxide and acid, and carburetted hydrogen are evolved, and a little charcoal, with a trace of oily matter, is deposited. Hydrochloric acid dissolves oxalic acid without decomposition. Mixed with about 20 parts of sulphuric acid, and gently heated, it is rapidly resolved into equal volumes of carbonic acid and carbonic oxide, which gases are evolved, whilst the water of the crystals remains combined with the sulphuric acid. Oxalic acid absorbs chlorine, and the resulting compound is resolved by the action of water into hydrochloric and carbonic acids. (*Ann. de Ch. et Ph.*, xix. 84.) The intensity of the acidity of oxalic acid is such, that 1 part in 200000 of water reddens litmus. It abstracts lime from sulphuric acid when added to a solution of sulphate of lime, but oxalate of lead is decomposed by sulphuric acid, so that its affinity for bases appears to be about equal to that of sulphuric acid. It is extremely poisonous, and many accidents have occurred from its resemblance in external appearance to Epsom salt (sulphate of magnesia) and from the carelessness with which medicines are often dispensed and taken. The intense sourness of oxalic acid, and the saline bitterness of the sulphate, readily distinguish them; chalk or whiting, or magnesia or carbonate of magnesia, or large draughts of soap and water, are the most ready antidotes.

The composition of oxalic acid is a subject which has engaged much attention, since Döbereiner first suggested the non-existence of hydrogen as one of its ultimate elements, and showed that in its *anhydrous* state, as it exists in combination with certain bases, as, for instance, with oxide of lead, it might be regarded as a binary compound of carbon and oxygen. Its equivalent, founded upon this view, is 36, and it consists of ($2 \text{ Car} + 3 \text{ O}$), or,

Carbon	2	12	33.33	or	Carbonic oxide	1	14	38.9
Oxygen	3	24	66.67		Carbonic acid	1	22	61.1
Oxalic acid	1	36	100.00			1	36	100.0

The ordinary crystals contain

							Berzelius.	Prout.
Anhydrous oxalic acid.	1	36	57.14	58	57.15			
Water	3	27	42.86	42	42.85			
Crystallized oxalic acid	1	63	100.00	100	100.00			

And the crystals, dried as far as possible without decomposition, by which they lose about 28 per cent. of water, leave a compound of

				Berzelius.	
Anhydrous oxalic acid	1	36	80	80.5	
Water	1	9	20	19.5	
	1	45	100	100.0	

Those who consider an atom of water as an essential component of the dry oxalic acid, represent it by the equivalent 45, and regard the acid as a compound of

Carbon	2	12	26.67
Oxygen	4	32	71.11
Hydrogen	1	1	2.22
	1	45	100.00

OXALATE OF AMMONIA.—This curious salt is generally obtained by saturating a solution of oxalic acid by ammonia, and crystallizing. It forms prismatic crystals, (BROOKE, *Ann. of Phil.*, N. S., vi. 374,) of which 45 parts require 1000 of cold water, for their solution. They are much more soluble in hot water. Added to any soluble compound of lime, this salt produces an insoluble *oxalate of lime*, provided no excess of acid be present; hence its use as a test of the presence of lime in water. The crystals are insoluble in alcohol. They contain 2 equivalents of water, 1 of which may be expelled by heat, when they crumble into a white powder, composed of

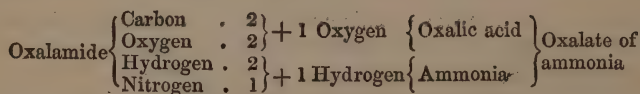
				Berzelius.	Berard.	Thomson.
Ammonia	1	17	27.42	26.88	27.66	25.55
Oxalic acid	1	36	58.06	59.37		
Water	1	9	14.52	13.75	72.34	74.45
Oxalate of ammonia	1	62	100.00	100.00	100.00	100.00

BINOXALATE OF AMMONIA ($2\text{Ox} + \text{A}$) is less soluble than the oxalate; it consists of 2 proportionals of acid, 1 of ammonia, and 2 of water (BERARD), 4 of water (DUMAS).

OXALAMIDE. OXAMIDE.—When oxalate of ammonia is distilled, it becomes opaque from loss of water, fuses, boils, decomposes, and volatilizes, leaving a little carbon behind; the liquid which passes over contains a flocculent substance, which also lines the neck of the retort, and to which M. Dumas has given the name of *oxalamide*; it may be separated by washing and filtration, 100 parts of the oxalate yielding about 5. The other products are ammonia, water, carbonic acid, carbonic oxide, and cyanogen. Oxalamide is in imperfect crystallized plates, or a granulated powder, without taste or smell, and having no action on test-papers. It is volatile when carefully heated, but generally sublimes with more or less decomposition, yielding cyanogen and carbon: it is scarcely soluble in water at 60° , and a saturated solution at 212° deposits it in crystalline flocculi. It is insoluble in alcohol. It is composed of

				Dumas.
Carbon	2	.	12	7.4
Oxygen	2	.	16	36.3
Hydrogen	2	.	2	4.5
Nitrogen	1	.	14	31.8
<hr/>				
Oxalamide	1		44	100.0

Consequently oxalamide differs from oxalate of ammonia in containing less water, by 2 atoms; for 44 oxalamide + 18 water = 62 oxalate of ammonia; and oxalamide may, under certain circumstances, resume this elementary water, as by the action of acids or hydrated alkalis aided by heat. Boiled with potassa, or soda, oxalamide evolves ammonia, and the carbon and oxygen remain in the state of oxalic acid: the dilute sulphuric, nitric, and hydrochloric acids convert it into oxalic acid, and become ammoniacal salts. Boiled with concentrated sulphuric acid, oxalamide affords sulphate of ammonia, and equal volumes of carbonic acid and carbonic oxide are disengaged: concentrated nitric acid converts oxalamide into nitrate of ammonia and carbonic acid. In these cases, oxalamide, by decomposing an atom of water, furnishes oxalic acid and ammonia, or



The elements of oxalamide, as will be seen by the above diagrams, are such as to represent 2 atoms of carbonic oxide + a compound of 2 atoms of hydrogen and 1 of nitrogen; now it has been ingeniously suggested by Dumas that an analogy subsists between this bihydruret of nitrogen, and the bicarburet of nitrogen or cyanogen, and that both resemble the haloid bases; that is, considering $n+2h$, which we may call *ammogen*, as a compound analogous to cyanogen, *oxamide* would be a compound analogous to the cyanurets and chlorides. We shall afterwards have occasion to revert to this analogy; in the mean time, it may be observed that the elements of oxalamide are such as to admit of other hypothetical distributions; that they are, for instance, equivalent to nitrous oxide and olefiant gas ($n+2o$) + ($2h+2car$), or to cyanogen and water ($n+2car$) + ($2h+o$). Compounds of the base $n+2h$ with other acids are also distinguished by the termination *amide*, as *benzamide*, *succinamide*, &c.

OXALATE OF POTASSA ($2Ox' + P$) forms flat rhomboidal crystals, soluble in rather less than 3 parts of water at 60° : the crystals include 1 proportional of water. The greater number of vegetable substances, such as cotton, wood, sugar, starch, gum, and most of the acids, and some animal substances, yield oxalic acid when fused with from four to six times their weight of caustic potassa, at a temperature below that which occasions charring: in this way *oxalate of potassa* is produced, and is converted, at a higher temperature, into carbonate of potassa.

BINOXALATE OF POTASSA. ($2Ox' + P$).—Oxalate of potassa, dissolved in oxalic acid, produces the *binoxalate*, which crystallizes in small rhombic crystals of a bitterish and sour taste, soluble in about 10 parts of cold water. This salt, together with the quadroxalate, exists ready formed in the juice of the *Oxalis acetosella*, and is known under the name of *salt of wood sorrel*.

QUADROXALATE OF POTASSA. ($4Ox' + P$).—When binoxalate of potassa is digested in nitric or hydrochloric acid, half the potassa is abstracted and a *quadroxalate* remains. The crystals of this salt include

7 proportionals of water: or, according to Berard, only 3. The composition of these several oxalates of potassa was originally pointed out by Wollaston, and deserves to be recorded as the first well-authenticated illustration of the theory of multiple proportionals. (*Phil. Trans.*, 1808.)

AMMONIO-OXALATE OF POTASSA.—When the binoxalate of potassa is neutralized by an atom of ammonia, a double salt, which forms long, permanent, acicular crystals, is obtained.

OXALATE OF SODA is sparingly soluble in water, and separates from its solution in small crystalline grains, composed of

				Berard.	Thomson.
Soda ₁	1	32	41·6	41·08	36·37
Oxalic acid	1	36	46·7	58·92	63·63
Water	1	9	11·7		
Oxalate of soda	1	77	100·0	100·00	100·00

There is a *binoxalate*, but apparently no *quadroxalate* of soda.

OXALATE OF LITHIA is difficultly crystallizable and very soluble. The *binoxalate* forms small transparent granular crystals, not so soluble as the neutral salt.

OXALATE OF LIME. ($Ox' + C.$)—This compound exists in many plants, and the little transparent bodies called *raphides*, found in the cellular tissue, and floating occasionally in their juices, as in the sap of very old trees, and in the juice of the common hyacinth, are composed, according to Raspail, of this salt. Oxalate of lime also exists occasionally in the human urine, and forms calculi of the kidney and bladder, which, from their rough or nodular exterior and brown colour, are generally called *Mulberry calculi*. It may be formed artificially by adding oxalic acid or oxalate of ammonia to any solution of lime. It is insoluble in water, and in excess of oxalic acid, but dissolves in hydrochloric and nitric acids: hence in testing *acid solutions* for lime, by oxalic acid, or oxalate of ammonia, the excess of acid should be previously neutralized. Whilst drying upon the sand-heat this salt becomes singularly electrical. At a red heat it is converted first into carbonate, and then into quicklime. When recently precipitated, well washed, and dried by mere exposure to air, it consists of

				Thomson.
Lime	1	28	34·1	33·98
Oxalic acid	1	36	43·9	43·69
Water	2	18	22·0	22·33
<hr/>				
Dried at 60°	1	82	100·0	100·00

When kept at 212°, till it no longer loses weight, it appears to consist of

				Vogel.	Berard.	Gay Lussac and Thenard.
Lime	1	28	38·4	38·5	38	38·655
Oxalic acid	1	36	49·3	49·5	62	61·345
Water	1	9	12·3	12·0		
Dried at 212°	1	73	100·0	100·0	100	100·000

When dried at 500° , it becomes *anhydrous*, and then contains

				Vogel. Thomson.	Dumas.
Lime	1	28	43.7	43.75	44.01
Oxalic acid .	1	36	56.3	56.25	55.99
<hr/>				<hr/>	<hr/>
Dried at 500°	1	64	100.0	100.00	100.00

As oxalate of lime is frequently referred to in quantitative analysis, the degree of desiccation must be, in such cases, attentively observed; but it is perhaps better to convert it by heat and sulphuric acid into *anhydrous sulphate of lime*, the equivalent of which is more certain.

"A compound of chloride of calcium with oxalate of lime, containing water of crystallization, is obtained in good crystals, which are persistent in the air, by dissolving oxalate of lime to saturation in hot hydrochloric acid, and allowing the solution to cool; it consists of 1 equivalent of each salt with 7 equivalents of water. Oxalate of lime is known to combine with 2 equivalents of water, of which 1 appears to remain in this double salt, while the other is replaced by chloride of calcium, carrying its 6 atoms of water of crystallization along with it." (GRAHAM.)

OXALATE OF BARYTA is very nearly insoluble. It cannot be obtained in an anhydrous state, but when dried at 212° , contains

					Berard.
Baryta	1	77	63.1	} Water	62.17
Oxalic acid . .	1	36	29.5		37.83
Water	1	9	7.4		
Oxalate of baryta	1	122	100.0		100.00

BINOXALATE OF BARYTA is formed by boiling excess of oxalic acid with carbonate or nitrate of baryta; on cooling it is deposited in transparent crystals. Boiling water resolves these into a precipitate of neutral oxalate, and free acid. The crystals contain

					Berard.	
Baryta	1	77	46.1	} . . .	45	
Oxalic acid . .	2	72	43.1			
Water	2	18	10.3			
<hr/>						
Binoxalate of baryta	1	167	100.0		100	

OXALATE OF STRONTIA is a white tasteless powder nearly insoluble in water, (in 1920 boiling water, HOPE.) It consists of 1 atom of oxalic acid, 1 of strontia, and 2 of water. (THOMSON.)

OXALATE OF MAGNESIA is a white, tasteless, and almost insoluble powder; yet it is not immediately thrown down when oxalic acid, or even oxalate of ammonia, is added to sulphate of magnesia, unless the solutions are concentrated and hot. Hence oxalate of ammonia may be used to detect lime in solutions containing magnesia.

OXALATE OF MANGANESE.—When black oxide of manganese and superoxalate of potassa are triturated together and moistened, carbonic acid is evolved; and, on adding more water, and filtering, a red solution, containing oxalic acid, potassa, and manganic acid, is obtained, which after a time becomes colourless, and a triple salt is formed, containing the protoxide of manganese. Oxalic acid and oxalate of ammonia throw

down a white powder from concentrated solutions of the protosalts of manganese.

OXALATE OF IRON.—The *protoxalate* crystallizes in green prisms, and may be formed either by digesting the metal, or dissolving the protoxide in the acid. The *peroxalate* is thrown down from the perhydrochlorate or persulphate of iron, in the form of a difficultly-soluble yellow powder, which is taken up again by excess of oxalic acid: hence the use of this acid in removing iron-moulds, which it does without injuring the texture of linen. Pure ferrocyanuret of iron is soluble in oxalic acid, and this solution diluted with water is used by Mr. Stephens as a writing fluid. When oxalic acid is present in very dilute solutions of iron, the precipitation of the iron by ferrocyanuret of potassium is prevented. (J. T. COOPER.)

OXALATE OF ZINC is formed by adding oxalic acid to a soluble salt of zinc: it is a white powder, nearly insoluble.

OXALATE OF TIN is formed, according to Bergman, by digesting the metal in the acid; the solution, slowly evaporated, gives prismatic crystals.

OXALATE OF CADMIUM is a white insoluble powder.

OXALATE OF COPPER.—Oxalic acid oxidizes and dissolves copper. When oxalic acid is added to sulphate or nitrate of copper, *oxalate of copper* is thrown down in the form of a green powder, soluble in excess of acid, and yielding a solution from which prismatic green crystals may be obtained, of binoxalate?

OXALATE OF COPPER AND AMMONIA.—This, and several other *double oxalates of copper*, have been described by Vogel. (*Schweigger's Journal*, vii.) By digesting oxalate of copper in a solution of oxalate of ammonia, and filtering, rhomboidal crystals were obtained on evaporation, which detonated when suddenly heated: when slowly heated, they merely lost water and ammonia. From the analysis of this salt, it appears to consist of

						F. C. Vogel.
Ammonia . . .	1	. . .	17	. . .	10.90	. . . 10.5
Oxide of copper	1	. . .	40	. . .	25.64	. . . 25.0
Oxalic acid . . .	2	. . .	72	. . .	46.15	. . . 47.5
Water . . .	3	. . .	27	. . .	17.31	. . . 17.0
	1		156		100.00	100.0

By digesting oxalate of copper in caustic ammonia, and pouring the solution thus obtained into a shallow basin, it deposits flat six-sided prisms of a blue colour, which effloresce on exposure to air. The undissolved portion of the oxalate also combines with ammonia, and produces another distinct compound.

OXALATE OF COPPER AND POTASSA is obtained by digesting carbonate of copper in solution of binoxalate of potassa. Prismatic and rhomboidal crystals are formed, which Vogel considers as two distinct salts; the former, consisting of 1 proportional of oxalate of copper, 1 of oxalate

of potassa, and *eight* of water; and the latter, of 1 proportional of oxalate of copper, 1 of oxalate of potassa, and *two* of water.

OXALATE OF COPPER AND SODA.—Vogel has also described two varieties of this salt. (*Schweigger's Journal*, vii.)

OXALATE OF LEAD ($Ox' + Pl$) is thrown down in crystalline grains on adding oxalic acid to nitrate of lead. It is insoluble in water, but dissolves sparingly in excess of oxalic acid. Heated in close vessels it leaves a suboxide of lead; in the air it leaves oxide of lead: when heated in a tube with potassium, it detonates violently: it is anhydrous when dried at 212° , and consists of

										Berzelius.
Oxide of lead	1	.	.	112	.	.	75.68	.	.	75.46
Oxalic acid	.	1	.	36	.	.	24.32	.	.	24.54
	1			148			100.00			100.00

OXALATE OF ANTIMONY has not been examined.

OXALATE OF BISMUTH is deposited in crystalline grains, when solution of oxalic acid is dropped into nitrate of bismuth.

OXALATE OF COBALT is an insoluble red powder, precipitated by oxalic acid from solutions of cobalt. It dissolves in excess of oxalic acid, and the solution furnishes crystals. The dry salt yields, when heated in a tube, 0.3286 metallic cobalt, 0.4757 carbonic acid, and 0.1957 water; it therefore consists of 1 atom of oxide of cobalt, 1 of oxalic acid, and 2 of water. When carefully heated, it loses water, and then burns in the air. (DÖBEREINER.) It forms a double salt with oxalate of ammonia.

OXALATE OF URANIUM is difficultly soluble in water, and is precipitated by concentrated oxalic acid from the neutral salts of uranium. A weak solution of a salt of uranium is not disturbed by oxalate of potassa. The oxalate of uranium contains 13.5 per cent. water, the oxygen of which is to that of the oxide as 3 to 1. (BERZELIUS.)

OXALATE OF CERIUM is precipitated by the addition of oxalic acid or oxalate of ammonia to solutions of the protoxide of cerium, of a white colour, insoluble in excess of acid, but soluble in liquid ammonia. In solutions of the peroxide of cerium, the precipitate is of a dingy red, and soluble in ammonia.

OXALATE OF NICKEL is thrown down from the nitrate in the form of an insoluble green powder. It contains 13.4 per cent. (= 2 atoms) of water: heated in a retort it yields carbonic acid and metallic nickel: it forms double salts with the oxalates of ammonia, potassa, and soda.

OXALATE OF CHROMIUM, in solution, is red by transmitted, and green by reflected light; it yields, on evaporation, a green deliquescent and very soluble salt, which crystallizes with excess of acid, and is not precipitated by, but forms double salts with, the alkalis.

OXALATE OF MOLYBDENUM.—The *protoxalate* is dark-gray; black when dry; and little soluble in excess of oxalic acid. The *peroxalate* may be obtained in very dark-blue crystals, yielding a red solution from

which ammonia throws down a red *basic* salt, insoluble in excess of ammonia. Molybdic acid yields a colourless solution in oxalic acid, which, when evaporated, becomes at first gelatinous, and then crystalline; it is soluble in water and alcohol. These oxalates of molybdenum all yield double salts with oxalate of potassa. (BERZELIUS.)

OXALATE OF TITANIUM falls as a curdy hydrated precipitate, when a solution of titanium is heated with oxalic acid: it dissolves in excess of acid, and consists, according to Rose, of 6 atoms of oxide of titanium, 1 of oxalic acid, and 6 of water.

OXALATE OF COLUMBIUM.—According to Wollaston, the recently-precipitated hydrated columbic acid dissolves in oxalic acid; but Gahn, Berzelius, and Eggertz state, that only a trace of the acid is so dissolved, but that binoxalate of potassa readily takes it up and forms with it a double salt, from which the alkalis throw down columbic acid.

OXALATE OF MERCURY is precipitated from the nitrates by oxalic acid. The *protoxalate* is scarcely soluble, and detonates slightly when heated. It was once supposed to exist in Howard's fulminating mercury, but this is not the case. It forms a double salt with oxalate of potassa.

OXALATE OF SILVER is an insoluble white powder, which blackens when exposed to light. It is precipitated on adding oxalic acid to nitrate of silver, and is soluble in nitric acid. It detonates slightly when violently struck upon an anvil: when heated it becomes electric, and evolves water and carbonic acid, leaving metallic silver. It forms a double salt with oxalate of potassa.

OXALATE OF ALUMINA is easily formed by dissolving the newly-precipitated earth in oxalic acid: it does not crystallize, but affords, on evaporation, a gelatinous mass, which deliquesces on exposure. This is probably a binoxalate, for Berzelius states that the neutral oxalate is insoluble.

HYDROXALIC ACID. SACCHARIC ACID. (*Acide oxalhydrique.*)—Under this name Guérin-Varry (*Ann. de Ch. et Ph.*, lii. 318) has described a peculiar acid, which is formed, together with oxalic acid, during the action of nitric acid upon sugar, gum, and other substances, and which was noticed by Scheele, and considered as identical with malic acid. Guérin obtains this acid by mixing 1 part of gum arabic with 2 of nitric acid, diluted with half its weight of water in a retort of four times the capacity of that of the mixture, and connected with a tubulated receiver: heat is applied till nitrous vapours begin to appear; it is then withdrawn, and a large quantity of nitrous gas succeeds; when this ceases, the liquor is boiled for an hour, then diluted with 4 parts of water, saturated by ammonia, and a solution of nitrate of lime is then added to precipitate oxalic acid: the solution, which is now of an orange colour, is filtered and precipitated by acetate of lead: the precipitate is washed upon a filter till the washings no longer are discoloured by sulphuretted hydrogen, and is then decomposed either by a stream of that gas or by sulphuric acid diluted with 6 weights of water: the acid thus obtained is evaporated

by a gentle heat, and, when sufficiently concentrated, is neutralized by ammonia, and evaporated till it begins to crystallize. The crop of crystals which it affords, and which are dark coloured, are dissolved and treated by animal charcoal; the decoloured solution is then precipitated again by acetate of lead, and the precipitate is decomposed as before: the acid liquor now obtained is cautiously evaporated till it acquires the consistency of syrup, and the evaporation is completed, in vacuo, till the residuary liquor begins to acquire a yellow tint.

Trommsdorf's process for obtaining this acid is as follows:—He heats a mixture of equal parts of sugar and nitric acid (specific gravity 1·2) till it begins to effervesce; abundance of gas is evolved, and the liquid becomes thick and yellow; it is then diluted with water, and saturated by chalk, the excess of which, and the precipitated oxalate of lime, are removed by filtration; the filtered liquor is concentrated by evaporation and mixed with alcohol, which precipitates the *hydroxalate of lime*: this is collected, redissolved, filtered through charcoal, and decomposed by acetate of lead; the resulting *hydroxalate of lead* is decomposed as before by sulphuretted hydrogen: to get it colourless, the acid must be saturated by soda, again thrown down by lead, and this decomposed as before. 8 ounces of sugar yield about 1 ounce of the acid. (*Ann. de Ch. et Ph.*, liv. 208.)

Hydroxalic acid, when obtained in its utmost state of concentration, is in the form of a syrupy, colourless, inodorous, and intensely-sour liquid. Its specific gravity is 1·415 at 60°. It unites in all proportions with water and alcohol, but is only sparingly soluble in ether. It is very deliquescent. It precipitates lime, baryta, and strontia water, and the precipitates are all soluble in excess of acid: in this respect it resembles tartaric acid; but it differs from that acid in not precipitating potassa or its salts when added to them in excess: it is distinguished from malic acid, which does not precipitate the above bases. It furnishes copious white precipitates in solutions of lead and silver. It dissolves zinc and iron, with disengagement of hydrogen, but has no action on tin. When 1 part of hydroxalic acid and 3 of nitric acid are mixed and left for a month, at common temperature, being shaken daily, nitrous gas and carbonic acid are evolved, and crystallized oxalic acid formed: boiled with nitric acid, hydroxalic acid is converted into oxalic and carbonic acids: with equal parts of sulphuric acid and water it yields sulphurous and carbonic acids; it is changed into formic acid when gently heated with sulphuric acid and black oxide of manganese. Subjected to destructive distillation it affords the usual products of these compounds, and leaves a bulky charcoal.

According to Guérin, this acid, in its *anhydrous* state, as in the salt of lead, is composed of ($4\text{ car} + 3\text{ h} + 6\text{ o}$): its equivalent, therefore, is 75; or

				Guérin.
Carbon	4	24	32	32·4
Hydrogen	3	3	4	3·9
Oxygen	6	48	64	63·7
Anhydrous hydroxalic acid	1	75	100	100·0

The above numbers are, it is to be observed, equivalent to 2 atoms of

dry oxalic acid + 3 atoms of hydrogen, or to 1 atom of tartaric acid + 1 atom of water. (See a later paper on this acid, called *Saccharic acid*, by THAULOW, *Ann. de Ch. et Ph.*, Lxix. 52, who gives as the formula of this acid ($12\text{ car} + 5\text{ h} + 11\text{ o}$) + 5 q , in its state of hydrate.)

III. CITRIC ACID.—This acid exists in many vegetables, either free, or combined with lime: it is especially abundant in *lemon-juice*, from which it was first obtained in a crystalline form by Scheele: it is contained in currants, gooseberries, raspberries, and other fruits, and is often associated with malic acid.

Citric acid is obtained from lemon or lime juice as follows:—Boil the expressed juice for a few minutes, and, when cold, strain it through fine linen; then add powdered chalk as long as it produces effervescence; heat the mixture, and strain as before: a quantity of *citrate of lime* remains upon the strainer, which, having been washed with cold water, is to be put into a mixture of sulphuric acid with 20 parts of water: the proportion of acid may be about equal to that of the chalk employed. In the course of 24 hours, the citrate of lime will have suffered decomposition, and sulphate of lime is formed, which is separated by filtration. The filtered liquor, by careful evaporation, as directed for tartaric acid, furnishes crystallized citric acid.

The preparation of this acid is carried on by a few manufacturers upon an extensive scale; in different states of purity, it is employed by the calico-printers, and used for domestic consumption. Many circumstances which have not here been alluded to, are requisite to ensure complete success in the operation; these have been fully described by Mr. Parkes, in the third volume of his *Chemical Essays*. The average proportion of citric acid afforded by a gallon of good lemon-juice, is about 8 ounces. Dr. Henry states that he has obtained as much as 12 ounces.

Citric acid forms beautiful crystals, of which the primary form is a right rhombic prism. They have a very sour taste, and are soluble in somewhat less than their own weight of water at 60° , and in half their weight at 212° . They also dissolve in alcohol.

M. Tilloy, of Dijon, recommends currants as a source of citric acid: they are bruised, and the expressed juice is fermented, and then distilled to obtain the alcohol: the residue is saturated by chalk, and the washed citrate of lime decomposed by sulphuric acid: from 100 parts of currants he obtained 10 of alcohol and 1 of acid. (*Ann. de Ch. et Ph.*, xxxix. 222.)

Citric acid is sometimes fraudulently mixed with the tartaric: the adulteration may be discovered by gradually adding to the acid dissolved in water, a solution of carbonate of potassa, which will occasion the precipitation of bitartrate of potassa if tartaric acid be present.

The crystals of citric acid include a certain proportion of water, part of which may be expelled by heat: in its *anhydrous* state, as it exists combined with certain bases, it is a compound of

				Berzelius.	
Carbon	4	24	41.38	41.369	
Hydrogen	2	2	3.45	3.800	
Oxygen	4	32	55.17	54.831	
<hr/>				<hr/>	
Anhydrous citric acid	1	58	100.00	100.000	

Hence we have the equivalent of this acid 58, (58.48 TURNER, 58 GMELIN,) or $(4car + 2h + 4o)$.

The crystals of citric acid, deposited from its saturated solution at 212° , contain 1 atom of water: they are, therefore, represented by the formula $(4car + 2h + 4o) + q$, or $(cit' + q)$. Their equivalent is $58 + 9 = 67$, and they include

				Dumas.	Prout.	Ure.
Carbon	4	24	35.8	36.28	34.28	33.00
Hydrogen	3	3	4.5	4.45	4.76	4.63
Oxygen	5	40	59.7	59.27	60.96	62.37
Crystallized citric acid	1	67	100.0	100.00	100.00	100.00

These crystals fuse at a little above 212° , into a limpid liquid, without loss of weight, and concrete, on cooling; into a solid transparent mass. The crystals which are obtained by the *spontaneous evaporation*, at common temperatures, of a solution of citric acid, differ in composition from the former, and contain 3 atoms of anhydrous acid and 4 of water ($3cit' + 4q$), which, therefore, is the composition of the ordinary citric acid of commerce; or

				Berzelius.
Anhydrous citric acid	1	58	82.86	83
Water	$\frac{4}{3}$	12	17.14	17
Common crystallized acid	1	70	100.00	100

These crystals are permanent at common temperatures, but when dried at 212° they effloresce and lose exactly half their weight of water, being reduced to $(3cit' + 2q)$, or

				Berzelius.
Anhydrous citric acid	1	58	90.6	90.7
Water	$\frac{2}{3}$	6	9.4	9.3
Effloresced citric acid	1	64	100.0	100.0

When any attempt is made to drive off more water by the application of a higher temperature, the acid is itself decomposed.

CITRATES.—The *neutral* citrates, considered as compounds of anhydrous citric acid and bases, are so constituted that the oxygen in the acid is to that in the base as 4 to 1. Many of them are insoluble, or difficultly soluble, but are soluble in excess of acid: those which are soluble do not deposit difficultly-soluble acid citrates, when excess of acid is added. When cold, they give scanty precipitates with the salts of lime, but copious when heated: these precipitates are soluble in a large quantity of water, and in acetic acid. Some of the peculiarities of the citrates have been pointed out by Berzelius. (*Ann. de Ch. et Ph.*, Lii. 424 and 432.)

CITRATE OF AMMONIA crystallizes with difficulty in prisms.

CITRATE OF POTASSA is very soluble, deliquescent, and difficultly crystallizable. It is much used in medicine as a mild diaphoretic, and is the *Salt of Riverius* of old pharmacy. 76 parts of the crystallized acid saturate 70 of carbonate of potassa.

CITRATE OF SODA is crystallizable in prisms, of a saline flavour, and soluble in somewhat less than their weight of cold water. When this

salt is dried at 212° it loses 17.5 per cent. of water, and the remaining salt is a compound of ($cit' + S + q$). Berzelius conceives that when this salt is dried at 200° (centigrade) it not only loses its water of crystallization, but also a portion of water derived from the elements of the acid; but that, notwithstanding this partial decomposition, it reverts to the state of perfect citrate of soda, when redissolved in water.

CITRATE OF LITHIA is very difficultly soluble, and does not crystallize.

CITRATE OF LIME has been adverted to in the preparation of citric acid. It is nearly tasteless, and scarcely soluble in water, but readily soluble in solution of citric acid: when moistened, it soon grows mouldy if exposed to air. Neutral citrate of lime, dried at 212° , consists of ($cit' + C + q$), or

				Berzelius.	Gay Lussac and Thenard.
Lime . . .	1 . . .	28 . . .	29.5 . . .	29.70	31.17
Citric acid . .	1 . . .	58 . . .	61.0 . . .	60.93	68.83
Water . . .	1 . . .	9 . . .	9.5 . . .	9.37	
Citrate of lime	1	95	100.0	100.00	100.00

This salt is sometimes prepared in, and exported from, countries where lemons and limes are abundant, as a source of citric acid.

CITRATE OF BARYTA, when neutral, is very difficultly soluble. The *bicitrate* forms acicular crystals, soluble in water and efflorescent. The neutral citrate is represented by ($cit' + B + 2q$).

CITRATE OF STRONTIA.—Citric acid renders strontia water turbid. Citrate of potassa does not precipitate nitrate of strontia, till heated.

CITRATE OF MAGNESIA is difficultly soluble, and does not crystallize.

CITRATE OF MANGANESE is formed by digesting moist protoxide of manganese in citric acid; it produces white arborescent crystals. Carbonic acid is evolved from a mixture of citric acid and peroxide of manganese.

CITRATE OF IRON.—According to Dr. Henry (*Elements of Chemistry*, 9th edition, ii. 200), citric acid dissolves iron-filings with effervescence, and forms a nearly colourless solution, which deposits citrate of iron in the state of a white powder. It has a sweetish astringent taste; dissolves in water, but not in alcohol: and, when exposed in a moist state to the air, becomes first yellow, and then olive, being converted into a *percitrate* which is uncrystallizable and deliquescent. There is also a *bicitrate* of the protoxide, which is deposited in a white crystalline form during the solution of iron in excess of citric acid; it has a sour astringent taste, and is more permanent than the neutral protocitrate.

CITRATE OF ZINC.—Zinc dissolves in citric acid with effervescence: citric acid readily dissolves the oxide of zinc, and the solution deposits small crystals, scarcely soluble in water, and of an astringent taste.

CITRATE OF TIN.—Neutral citrate of potassa forms no precipitate either in protohydrochlorate or perhydrochlorate of tin.

CITRATE OF COPPER.—Citric acid forms a pale-blue precipitate in solution of sulphate and nitrate of copper. When solution of acetate of copper and citric acid are boiled together, a granular green precipitate gradually falls, composed of $(3 \text{ Cit} + 4 \text{ Cu} + 4 \text{ q})$. When dried at 212° it becomes blue, and loses half its water.

CITRATE OF LEAD is thrown down in the state of a nearly insoluble powder, when citric acid is added to nitrate of lead. According to Berzelius, a *neutral* citrate of lead is most certainly obtained by adding an alcoholic solution of citric acid to a solution of acetate of lead, and washing the precipitate with alcohol, for water abstracts part of its acid. It consists of $(\text{Cit} + \text{PL})$. On digesting this neutral salt with subacetate of lead, he obtained a bibasic salt, or *dicitrate of lead* $(\text{Cit} + 2 \text{ PL})$. By the action of ammonia on the neutral citrate he formed a subsalt, represented by $(3 \text{ Cit} + 4 \text{ PL})$: and lastly, by dissolving the neutral citrate of lead in hot and very weak nitric acid, the saturated solution deposited crystals on cooling, composed of $(3 \text{ Cit} + 2 \text{ PL} + 2 \text{ q})$.

CITRATE OF ANTIMONY?

CITRATE OF BISMUTH is an insoluble white compound.

CITRATE OF COBALT appears to be a soluble salt.

CITRATE OF URANIUM, formed by digesting oxide of uranium in citric acid, is a soluble and difficultly-crystallizable salt.

CITRATE OF NICKEL is not thrown down by adding either citric acid or citrate of potassa to the solutions of nickel.

CITRATE OF MERCURY.—Both the *protocitrate* and *percitrate* of mercury are insoluble, and thrown down when citric acid or a soluble citrate is added to the neutral solutions of mercury.

CITRATE OF SILVER is an insoluble white powder, which blackens when exposed to light. It detonates slightly when heated. It is the most uniform of the citrates, being always $(\text{Cit} + \text{Ag})$.

PYROCITRIC ACID.—When citric acid is distilled in a retort *per se*, an acid liquid is obtained, which, when saturated by lime, affords a precipitate, which may be decomposed by oxalic acid, and thus furnishes a peculiar product called, by Lassaigne, *pyrocitric acid*. (*Ann. de Ch. et Ph.*, xxi. 100.) See also a paper by Baup (*Ann. de Ch. et Ph.*, lxi. 182), *sur un nouvel acide citrique pyrogène, &c.* It forms salts, perfectly distinct from the citrates; its equivalent number is 56. It consists of $(5 \text{ car} + 2 \text{ h} + 3 \text{ o})$, or,

	Dumas.			
Carbon	5	30	53.6	54.07
Hydrogen	2	2	3.6	3.53
Oxygen	3	24	42.8	42.40
Pyrocitric acid	1	56	100.0	100.00

MALIC ACID.—The existence of a peculiar acid in the juice of *apples* was shown by Scheele, in 1785. He obtained it by adding solution of

acetate of lead to the expressed juice of unripe apples, by which a *malate of lead* was formed, and afterwards decomposed by sulphuric acid. Vauquelin obtained it by a similar process, from the juice of the *house-leek*. The same acid exists, according to Braconnot and Houton-Labillardière, in the berries of the *mountain-ash* (*Ann. de Ch. et Ph.*, viii. 214), from which it was first obtained by Mr. Donovan in 1815, and called by him *sorbic acid*; the apparent differences between the malic and sorbic acids are referable to the impurities of the former. Mr. Donovan has given the following process for its preparation. (*Phil. Trans.*, 1815.) Express the juice of the ripe berries, and add solution of acetate of lead, filter, and wash the precipitate with cold water; then pour boiling water upon the filter, and allow it to pass through the precipitate into glass jars: after some hours crystals are deposited, which are to be boiled with 2·3 times their weight of sulphuric acid; specific gravity 1·090. The clear liquor is to be poured off, and, while still hot, a stream of sulphuretted hydrogen is to be passed through it, to precipitate the remaining lead; the liquid is then filtered, and when boiled so as to expel the sulphuretted hydrogen, is a solution of the pure vegetable acid.

M. Braconnot procures this acid by saturating the juice of the scarcely-ripe berries with chalk; during evaporation malate of lime falls, which he decomposes by carbonate of soda; the malate of soda is decomposed by acetate of lead, and treated by sulphuretted hydrogen, as before described. (*Ann. de Ch. et Ph.*, vi.)

According to Liebig (*Ann. de Ch. et Ph.*, xliii. 259, and lii. 434), pure malic acid is obtained by boiling the juice with animal charcoal, filtering, adding a little potassa, evaporating, and adding alcohol to precipitate bitartrate of potassa: then distil off the alcohol, and reduce the residue to the consistency of syrup, and again add alcohol, which throws down mucilage. The residue of the second distillation, diluted and mixed with acetate of lead, yields *malate of lead*, which is washed and decomposed by sulphuretted hydrogen: to complete the purification of the acid, its solution is concentrated, diluted by alcohol, and half saturated by ammonia: the *bimalate of ammonia* is crystallized, and used as a source of *malate of lead*, to be decomposed as before.

Malic acid is usually obtained in the state of a colourless liquid, very sour, and scarcely susceptible of regular crystallization, though when very carefully evaporated it concretes into mamillary masses, showing traces of acicular crystals. It is deliquescent, and very soluble in alcohol and water. Nitric acid converts it into oxalic acid. Malic and citric acids, when *anhydrous*, are, according to Liebig, isomeric; malic acid is therefore represented by the equivalent 58, or ($4\text{car} + 2\text{h} + 4\text{o}$).

MALATES.—The neutral salts of the malic acid are composed of 1 atom of acid + 1 of base, and are not subject to those capricious modifications which characterize the citrates. The neutral malates are mostly soluble in water: those of ammonia, potassa, and soda, are very soluble, and deliquescent: the *bimalates* of those bases are less soluble, and are crystallizable: the neutral and bimalate of baryta are very soluble, and leave on evaporation gummy masses: the basic malate of baryta ($\text{mal} + 2\text{B}$) is insoluble. The neutral malate of strontia is soluble: the bimalate,

difficultly soluble. The same is the case with the corresponding salts of manganese. With peroxide of iron the neutral malate is uncrystallizable, soluble in water and alcohol, and deliquescent: the permalate of mercury is uncrystallizable; water resolves it into a super and a sub-salt. The best mode of distinguishing the malates is to convert them into *malate of lead*, which may be easily identified. (DUMAS.)

MALATE OF LIME.—The neutral malate ($mal' + C$) dissolves in 150 parts of water at 60° , and in 65 parts at 212° : the hot saturated solution deposits small crystals on cooling: its taste resembles that of nitre. According to Grotthus, it dissolves readily in solutions of other salts, such as those of nitrate of potassa, chloride of sodium and of calcium, and hydrochlorate of ammonia. The *bimalate of lime* ($2mal' + C$) dissolves in 50 parts of water at 60° , and yields flattened six-sided prisms, insoluble in alcohol: it exists in several plants, but when obtained from their juices it is disguised by mucilage.

MALATE OF MAGNESIA ($mal' + M$) forms permanent crystals, soluble in 28 parts of water.

MALATE OF LEAD ($mal' + PL$) is scarcely soluble in cold water: its hot saturated solution deposits white and brilliant lamellar crystals as it cools. When first thrown down as a precipitate, it appears pulverulent, but assumes spontaneously a crystalline aspect, especially when heated. It is fusible at 212° , and then becomes less easily soluble in water: to saturate boiling water with it, it must be added in fine powder, and in successive portions. It forms uncrystallizable double salts with malate of ammonia, and malate of zinc.

MALATE OF SILVER falls on mixing nitrate of silver with bimalate of ammonia; it is brilliant white, but becomes yellow when dried: it dissolves in boiling water, but by continued boiling it is reduced, and metallic silver separates.

PYROMALIC ACID.—According to Pelouze, malic acid enters into fusion at about 180° : at about 380° (176° Cent.) it is resolved into water, and two pyro-acids, which he terms *malæic* and *paramalæic acids*.

MALÆIC ACID is formed when malic acid is distilled at about 400° . A liquid passes over which crystallizes, and consists entirely of *malæic acid*; its taste is acid and nauseous: it is soluble in water and alcohol. The solution of this acid does not precipitate lime water: in a solution of acetate of lead it forms white flocculi, which gradually become semi-transparent. The anhydrous malæic acid consists of ($4car + h + 3o$), its equivalent being 49. From the experiments of Regnault, it appears that the malæic is identical with the equisetetic acid. (*Journ. de Pharm.*, xxiii. 30.)

MALÆATES.—These salts have not been much examined; they closely resemble the *succinates* in many of their properties.

PARAMALÆIC ACID is produced by the continuous action of a moderate heat upon the malæic acid; or by boiling it in a long tube, so that the evolved water constantly falls back upon the acid. This acid crystallizes

in large striated prisms, soluble in 200 parts of water, and of an acid flavour. The atomic composition of this acid is identical with the malæic. The properties of the paramalæic acid are the same as those of the acid found by Winckler in the juice of the *Fumaria officinalis*, and called by him *fumaric acid*. (*Ann. de Ch. et Ph.*, lvi. 429.) The same acid is also contained in Iceland moss, and was described by Pfaff under the name of *lichenic acid*. (*Ann. de Pharm.*, xvii. 148.)

PARAMALÆATES.—The *paramalæates* of ammonia, potassa, and soda, are very soluble and crystallizable: those of lime, baryta, and strontia, are also so far soluble that the acid affords no precipitate in their respective aqueous solutions. The paramalæate of peroxide of iron is insoluble and brown; that of copper, insoluble and green; and of lead, white, and not crystalline, except when deposited from its solution in boiling water. The paramalæate of silver is so insoluble that 1 part of the acid in 200,000 of water renders nitrate of silver turbid.

FORMIC ACID.—The peculiarities of an acid obtained by the distillation of *ants*, was first noticed by Fischer and Margraaf; but it was afterwards regarded as identical with acetic acid, upon the authority of Fourcroy and Vauquelin. (*Ann. de Chim.*, lxiv. 48.) Gehlen, however, (*Thomson's Annals*, v. 24,) and more lately Berzelius, have shown that it is a distinct compound; and Döbereiner has published some curious facts respecting its artificial production. (*Ann. de Ch. et Ph.*, xx. 329, and lii. 105.) He has shown that it is the result of the peroxidizement of several vegetable compounds, and that nascent oxygen converts citric and tartaric acids, and many other organic compounds, into formic acid: numerous other instances of the formation of this acid might be adduced.

Formic acid may be obtained from a mixture of tartaric acid, black oxide of manganese, and water; or more abundantly from a mixture of 2 parts of crystallized tartaric acid, 5 of peroxide of manganese, 5 of sulphuric acid, and 5 of water. Soon after mixture, these ingredients, which should be in a sufficiently capacious retort, effervesce violently, and give off abundance of carbonic acid; if afterwards distilled, the formic acid passes over, and may be concentrated in vacuo. Or, dissolve 1 part of sugar in 2 of water, and add 3 parts of powdered binoxide of manganese; heat the mixture to 140°, and then gradually add 3 parts of sulphuric acid previously diluted with its weight of water; violent effervescence ensues from the escape of carbonic acid, so that the distillatory apparatus must be very capacious, and the acid added gradually. When the violence of the effervescence is over, the mixture is to be agitated and distilled nearly to dryness; water, formic acid, and an etherine product pass over: this product is to be saturated with carbonate of lime and distilled to dryness, so as to yield formiate of lime. A pound of sugar affords formic acid adequate to the saturation of 5 or 6 ounces of carbonate of lime. To obtain the formic acid mix 7 parts of the formiate of lime with 10 of sulphuric acid diluted with 4 of water, and distil in a retort when the formic acid passes over. There are many other organic products which yield formic acid when similarly treated: among these, *salicin* is especially remarkable. (DÖBEREINER, *Ann. de Ch. et Ph.*, lii. 110.)

Formic acid possesses several peculiarities, which amply distinguish it from acetic acid, among which the most remarkable is the action of sulphuric acid, which converts it into water and carbonic oxide: and if sulphuric acid be poured upon *formiate of potassa*, which is a deliquescent and difficultly-crystallizable salt, of a saline bitter taste, an effervescence ensues, attended by the escape of *carbonic oxide* only.

Pure formic acid is best obtained by saturating the acid produced as above, by carbonate of soda, evaporating to dryness, and distilling 7 parts of the dry salt with 10 of sulphuric acid, and 4 of water. It has a pungent odour, and its combined water is only separable by uniting it to bases. It is a sour, colourless liquid, which boils at a little above 212° , without decomposition: its specific gravity is 1.1168. (GEHLEN.) It reduces the nitrate of silver and mercury, by simple ebullition. When highly concentrated, it is more caustic than sulphuric acid. (LIEBIG, *Journ. de Pharm.*, xxi. 381.)

The ultimate composition of formic acid, in its *anhydrous* state, is ($2\text{ car} + h + 3o$), and its equivalent is 37; or

				Berzelius.	Göbel.
Carbon	2	12	32.43	32.970	32.53
Hydrogen	1	1	2.70	2.807	3.06
Oxygen	3	24	64.87	64.223	64.41
<hr/>			<hr/>		
Anhydrous formic acid	1	37	100.00	100.000	100.00

These elements are equivalent to 2 atoms of carbonic oxide and 1 atom of water, into which formic acid is actually resolved by the action of sulphuric acid.

FORMIATES.—These salts are all soluble: they are resolved by heat into products which have not been particularly examined: they reduce the salts of silver, gold, platinum, and mercury by the aid of heat, and evolve carbonic oxide when acted on by sulphuric acid.

FORMIATE OF AMMONIA. (*for'* + A).—The ultimate components of the acid and base of this salt are ($2\text{ car} + h + 3o$) + ($n + 3h$); these elements are equivalent to *hydrocyanic acid* and *water*, or to ($2\text{ car} + n + h$) + $3(h + o)$. Döbereiner has shown, that simple distillation at a high temperature resolves formiate of ammonia into hydrocyanic acid and water; and Pelouze and Geiger have shown (*Ann de Ch. et Ph.*, xlviii. 585, and xlix. 286), that, under the influence of bases or acids and water, hydrocyanic acid is convertible into formic acid and ammonia.

The *formiates* of potassa, soda, lime, baryta, strontia, and magnesia, are crystallizable and soluble: that of alumina is uncrystallizable, and when its solution is boiled the base falls. The formiate of lead yields brilliant prismatic crystals, soluble in 36 parts of water at 55° , and consisting of 37 acid + 112 oxide. Formiate of copper crystallizes in greenish-blue hexagonal tables or prisms, efflorescent, soluble in 8.5 of water, and including 4 atoms of water + 1 anhydrous formiate.

SUBERIC ACID.—This acid was originally obtained by the action of nitric acid upon *cork*, by Brugnatelli. (*Crell's Annals*, 1787, i. 154.) It was afterwards examined by Bouillon-Lagrange (*Ann. de Chim.*, xxiii. 42), and more lately by Chevreul, Brandes, and Bussy.

Suberic acid is obtained as follows. (CHEVREUL, *Ann. de Ch. et Ph.*, lxii. 323.) Rasped cork is digested in 6 times its weight of nitric acid; it is slowly dissolved, and a fatty matter separates upon the surface: this is separated, and the solution evaporated at a gentle heat, and constantly stirred till it acquires a thick consistence; it is then diluted with 6 or 8 parts of water, and heated so as to separate an additional quantity of fat; the solution is then filtered and evaporated, and during cooling, oxalic acid and suberic acid are deposited; the latter in the form of a white powder: it may be purified by dissolving it in ammonia, precipitating the filtered solution by an acid, and washing the precipitate with cold water: it is sometimes purified by sublimation.

Suberic acid falls from its solution in hot water, in the form of a white powder, slightly acid, fusible at 300° , and subliming in acicular crystals: it dissolves in between 5 and 6 parts of anhydrous alcohol. The composition and equivalent of this acid, as given upon different authorities, are various: according to Bussy (*Jour. de Pharm.*, viii. 110, and xix. 425), anhydrous suberic acid is a compound of ($^s\text{car} + ^e\text{h} + ^3\text{o}$), and its equivalent is 78.

				Bussy.	Bouillon Lagrange.
Carbon	8	48	61.5	61.99	58.83
Hydrogen	6	6	7.7	7.59	7.67
Oxygen	3	24	30.8	30.42	34.00
Anhydrous suberic acid	1	78	100.0	100.00	100.00

SUBERATES.—These salts have been examined by Brandes. (*Schweiger's Jahrbuch*, II., III., and VI.) The *suberates* of potassa and of soda are soluble, deliquescent, and fusible without decomposition: those of ammonia, lime, baryta, strontia, magnesia, manganese, and alumina, are more or less soluble: the suberate of protoxide of iron is precipitated white; that of peroxide, brown: the suberates of zinc, tin, mercury, and silver, are also in the form of white precipitates: the suberates of cobalt, copper, and uranium, are red, blue-green, and yellow, and are insoluble. The suberate of lead and of silver are anhydrous, and consist of 78 acid + 112 oxide = (*sub'* + PL), and 78 acid + 116 oxide = (*sub'* + AG).

BOLETIC ACID.—This acid was obtained by Braconnot from the *Boletus pseudo-igniarius* (*Ann. de Ch.*, lxxx.), by cautiously evaporating its expressed juice to the thickness of syrup, digesting it in alcohol, dissolving the residue in water, and adding nitrate of lead to the aqueous solution; the precipitate, washed and diffused through water, was decomposed by sulphuretted hydrogen; the liquor was then filtered and evaporated till it formed crystals, which were purified by solution in alcohol and evaporation. These crystals are *boletic acid*; they are prismatic, and require 180 parts of water at 68° , and 45 of alcohol, for their solution, which reddens blues, and precipitates nitrate of lead, and the salts containing the peroxide, but not those of the protoxide of iron. This acid sublimes, with little alteration, when heated. Braconnot has examined the *boletates* of ammonia, potassa, lime, and baryta, but his researches have not as yet been confirmed by any other chemist.

FUNGIC ACID was procured also by Braconnot from the *Boletus juglandis*, and some other *fungi*; it is deliquescent and uncrystallizable. (*Ann. de Ch.*, LXXXVII.)

LICHENIC ACID apparently much resembles the boletic: it was obtained by Pfaff, by digesting lichen in a weak solution of carbonate of potassa, saturating this infusion with acetic acid, adding acetate of lead, filtering off the precipitate, and leaving the filtered liquor to itself: it slowly deposits crystals of *lichenate of lead*, from which *lichenic acid* was obtained by the action of sulphuretted hydrogen. This acid is soluble in water and alcohol, and forms acicular crystals, which are volatile when heated, without either fusion or decomposition. The *lichenates* of ammonia, potassa, and soda, are soluble and crystallizable; that of lime difficultly soluble; and those of baryta, strontia, zinc, manganese, and peroxide of iron, insoluble or nearly so. According to Schödlér the lichenic acid is the same as the paramalæic. (*Ann. der Pharm.*, xvii. 148.)

EQUISETIC ACID.—A peculiar acid combined with magnesia, was discovered by Braconnot in the *Equisetum fluviatile*. (*Ann. de Ch. et Ph.*, xxxix. 10.) According to Regnault it is identical with the malæic acid. (*Ann. de Ch. et Ph.*, LXII. 208.)

MOROXYLIC ACID, discovered by Klaproth in the bark of the *Morus alba*, or *white mulberry*. (*Nicholson's Journal*, vii.) An exudation was observed upon this bark, which proved to be a compound of a peculiar acid and lime, or a *moroxylate of lime*; its solution was decomposed by acetate of lead, and the *moroxylate of lead* thus obtained, decomposed by dilute sulphuric acid, furnished a solution of moroxylic acid, which gave acicular crystals on evaporation. This acid has the taste of succinic acid; it is soluble in water and alcohol, and does not, like some of its salts, form precipitates in metallic solutions. The quantity of this acid examined by Klaproth was so small, as to leave some doubt respecting its distinct nature.

VERDIC ACID.—This acid was extracted by Runge from several of the *Umbelliferæ* and *Plantagineæ*, &c., but chiefly from the root of the *Scabiosa succisa*, which, when dried, powdered, and digested in alcohol, yields a tincture from which ether throws down white flakes; these are dissolved in water, acetate of lead is added, and the precipitate decomposed by sulphuretted hydrogen. On evaporation a *yellow acid product* is obtained: in this state Berzelius proposes to call it *verdous acid*. When saturated by an alkali, and exposed to air, it absorbs oxygen and becomes *green*. (DUMAS, v. 416.) The further examination of these compounds may, perhaps, throw some light upon the nature of the green colouring-matter of leaves and plants.

BICOLORIC ACID. (TROMMSDORF, *Ann. der Pharm.*, xiv.; THOMSON'S *Organic Chemistry*, 96.)—A peculiar substance, obtained from the wood of the *Guilandina moringa*, or *Lignum nephriticum*, and extracted by Minor from the bark of the horse chestnut.

POLYGALIC ACID.—From the root of *Polygala senega*. (QUEVENNE, *Journ. de Pharm.*, xxii. 449.)

CAFFEIC ACID. (PFAFF, *Pogg.*, xxiv. 376; and THOMSON'S *Organic Chemistry*, 98.)—This acid was formerly described by Chenevix as the *bitter principle* of coffee. (*Phil. Mag.*, xii. 350.)

CRENIC ACID. **APOCRENIC ACID.** **PUTEANIC ACID.**—Acids found by Berzelius and by Haenlé in the ochrey deposits of certain spring-waters. (*Pogg.*, xxix.; and *Journ. de Pharm.*, xxi.)

CAHINCIC ACID.—Under this name Pelletier and Caventou have described an acid procured from the cortical part of the cahinca root: the plant belongs to the Rubiaceæ, and grows in Brazil, being used for the cure of intermittents, dropsy, and other diseases. The acid is obtained by dropping hydrochloric acid into a decoction of the root; it is gradually deposited in small crystals. It is more perfectly procured by evaporating a strong alcoholic tincture of the cahinca root to dryness, dissolving the residue in water, precipitating by lime, and decomposing the calcareous salt which falls by oxalic acid: the cahincic acid must then be purified by recrystallization.

Cahincic acid requires 600 parts of water for its solution; it is very soluble in alcohol, and the solution, if saturated when hot, deposits the acid in tufts of crystals as it cools. Ether dissolves it as sparingly as water: it is intensely bitter. When heated, it softens, chars, and yields a white crystalline sublimate, which is not bitter, and contains ammonia.

Cahincic acid is charred by sulphuric acid: with hydrochloric acid it forms a gelatinous compound, from which water throws down white flakes, which are not bitter: nitric and acetic acid produce very similar effects. With ammonia, potassa, lime, and baryta, it forms soluble neutral salts, which are not crystallizable, and from which the acids throw down cahincic acid. From Liebig's analysis (*Ann. de Ch. et Ph.*, xlvii. 186), this acid appears to consist of

Carbon . .	15	. .	90	. .	57.0
Hydrogen .	12	. .	12	. .	7.6
Oxygen . .	7	. .	56	. .	35.4
Cahincic acid	1		158		100.0

But its equivalent has not been determined by experiment.

[The organic acids not hitherto mentioned, are noticed under other heads.]

§ XVIII. VEGETABLE ALKALOIDS, AND SUBSTANCES ASSOCIATED WITH OR ALLIED TO THEM.

THE discovery of these substances is one of the most curious and important of modern chemistry. The first of them was detected in opium, in 1816, by Sertuerner of Einbeck, near Hanover. Several others were afterwards pointed out by Pelletier and Caventou, and among them *cinchonia* and *quinia* (in different species of *cinchona*), which have proved of so much use in medicine; more lately, several others have been added to the list. These *salifiable bases* appear all to contain *nitrogen* as one of their ultimate elements; they have a bitter taste, are for the most part

very sparingly soluble in water, more soluble in alcohol, and readily soluble in most of the dilute acids: with infusion of galls, and with excess of iodic acid, they furnish difficultly soluble precipitates; their compounds, with the acids, are decomposed and precipitated by the alkalis. They are mostly crystallizable, and are represented by very high equivalent numbers. They restore the blue colour to reddened litmus. They are found in plants united to certain *acids*, and usually forming neutral or acid salts, which, as well as their artificial combinations, are decomposed in the voltaic circle, and the base is evolved at the negative pole. Many hypotheses have been built upon the ultimate composition of these alkaloids, and some curious analogies pointed out respecting them by Liebig, Dumas, and others. A laborious analytical essay, having reference to the greater number of them, has been published in the *Ann. de Ch. et Ph.* (Lxviii. 113) by Regnault; but till organic analysis has made further progress, and has become more independent of hypothetical views, each experimentalist will necessarily differ somewhat from his predecessors.

In consequence of the analogy that pervades these principles, one general method of separating them is applicable to all, though each may require peculiar modifications of it. The substance which contains them is boiled in water acidulated by hydrochloric acid, the decoction is filtered and neutralized by ammonia, lime, or magnesia, the alkaloid is precipitated, and is then separated and purified.

I. MORPHIA: AND THE COMPONENT PARTS OF OPIUM.—The chemical examination of *opium* has been remarkably productive in interesting results. It has led to the discovery of several alkaloids, and of a peculiar acid with which they are combined; the substances which we shall have to describe under this head being the following: viz., morphia, narcotina, codeia, narceia, meconia, thebaia, and meconic acid.

Opium is the inspissated milky juice which flows from incisions made in the unripe seed-capsule of the poppy; it is only effectively obtained in warm climates, and is imported into this country chiefly from Turkey and India: it contains the above-mentioned substances, upon which its extraordinary medicinal powers depend, together with several others of little importance, such as gum, resin, extractive, ligneous matter, oil, and caoutchouc. Mulder analyzed five specimens of Smyrna opium with the following results. (THOMSON'S *Organic Chemistry*, 586.)

	1	2	3	4	5	Average.
Narcotina	6.808	8.150	9.360	7.702	6.546	7.713
Morphia	10.842	4.106	9.852	2.842	3.800	6.228
Codeia	0.678	0.834	0.848	0.858	0.620	0.767
Narceia	6.662	7.506	7.684	9.908	13.240	9.000
Meconia	0.804	0.846	0.314	1.360	0.608	0.790
Meconic acid . . .	5.124	3.968	7.620	7.252	6.644	6.121
Fat	2.166	1.350	1.816	4.204	1.508	2.209
Caoutchouc	6.012	5.026	3.674	3.754	3.206	4.338
Resin	3.582	2.028	4.112	2.208	1.834	2.753
Gummy extract . .	25.200	31.470	21.834	22.606	25.740	25.370
Gum	1.042	2.896	0.698	2.998	0.896	1.706
Mucus	19.086	17.098	21.064	18.496	18.022	18.733
Water	9.846	12.226	11.422	13.044	14.002	12.108
	97.852	97.504	100.858	97.252	96.666	97.836

1. MORPHIA.—The first step in the process for extracting morphia and the other alkaloids, consists in cutting the opium into small pieces, and digesting it in distilled water at the temperature of about 100° , till its soluble parts are completely extracted: it affords a clear brown infusion, smelling strongly of opium, and *acid* to tests. There are several modes of separating the morphia from it, but among them the two following are generally employed:—

a. The infusion of opium is concentrated by evaporation, and ammonia is dropped into it till that alkali is in slight excess; the precipitate which falls, and which is *chiefly* morphia and narcotina, is digested in *proof spirit*, at a temperature of about 130° , which dissolves the greater part of the colouring matter and narcotina: the morphia which remains is dissolved in boiling absolute alcohol, and separates in crystals on cooling and evaporation.

b. A better process for the extraction of these substances is that of Drs. Gregory and Robertson. The solution of opium is, if necessary, somewhat concentrated by evaporation, and a solution of pure chloride of calcium is added in sufficient quantity to precipitate all the sulphuric and meconic acids by which the alkaloids are held in solution: it is then filtered, evaporated to the consistency of syrup, and set aside to crystallize; the crystals are strongly pressed to squeeze out the mother-liquor, which contains resin, extract, narcotine, and other matters; the pressed crystals are then purified by treatment with animal charcoal and repeated crystallization, till they are obtained colourless: they consist of hydrochlorates of morphia and codeia: they are then dissolved in hot water, and ammonia is added, by which *morphia* is thrown down, and which, being separated by filtration, and dissolved in boiling alcohol, is obtained in pure crystals. The liquor from which the morphia has been precipitated, contains codeia in combination with sal-ammoniac, and some morphia: it is to be evaporated till it crystallizes, and the crystallized mass dissolved in a small quantity of water and decomposed by excess of caustic potassa; codeia is thrown down, and when dissolved in ether, may be procured crystallized by its evaporation.

The preceding, with some slight modifications and technical manipulation, is the best of the numerous processes which have been suggested for the preparation of morphia; of these, the reader will find an abstract in Dumas. (*Chim. app. aux Arts*, v. 770.)

Morphia, when obtained from its alcoholic solution, is in small brilliant and colourless crystals: they are generally six-sided prisms, with dièdral terminations, but their primary form is a right rhombic prism. According to Liebig these crystals are a *hydrate of morphia*. (*Ann. de Ch. et Ph.*, xlvii. 198.) When gently heated they become opaque and lose water: at a higher temperature morphia fuses into a yellow liquid, which becomes white and crystalline on concreting. In the air it burns with a bright resinous flame. Morphia, though apparently insoluble in cold water, has a very bitter taste: boiling water dissolves not more than a hundredth of its weight, but the solution is alkaline to delicate tests. It dissolves in 40 parts of cold, and 30 of boiling anhydrous alcohol. It is almost insoluble in ether; hence the method of separating it from narcotine, which is readily soluble in that menstruum. Morphia, according

to Wittstock, as quoted by Berzelius, is soluble in potassa and soda; hence the necessity of avoiding the use of those alkalis in its precipitation. Ammonia dissolves it sparingly, so that even that alkali ought not to be used in excess.

The quantity of morphia obtained from opium is variable; the produce is greatest from Turkey opium, and least from the East Indian and Egyptian. The average is generally estimated at about 1 oz. from the pound.

Much has been said respecting the methods of detecting morphia by tests: those which are commonly resorted to are nitric acid, which, when dropped upon crystallized morphia, forms a bright-red solution; and neutral perchloride of iron, which produces a very characteristic blue colour (or blue-green), when added to morphia, or to its salts, provided the solutions are not very dilute. Iodic acid is, according to Serullas, the best test of the presence of morphia; it produces a reddish-brown colour, and the odour of iodine is immediately perceptible. The minutest quantity of morphia has the property of decomposing iodic acid, but in cases where very small quantities are present it is recommended that a solution of starch should be employed to detect the free iodine; in these cases, however, I have always found the action of starch very equivocal.

Morphia, in its anhydrous state, is, according to Liebig, a compound of $(34\text{car} + 18\text{h} + 6\text{o} + \text{n})$, its equivalent being 284: or, in detail, as follows:—

			Liebig.	Brande.	Bussy.
Carbon	34	204	71·80	72·0	69·0
Hydrogen	18	18	6·34	5·5	6·5
Oxygen	6	48	16·90	17·0	20·0
Nitrogen	1	14	4·96	5·5	4·5
Anhydrous morphia	1	284	100·00	100·0	100·0

Crystallized morphia includes, according to Liebig, 2 atoms of water, and is consequently represented by the equivalent 302, or $(284 + 18)$. Other authorities transfer 1 atom of the water to the elementary composition of the morphia, and represent crystallized morphia as containing 1 atom of water only.

SALTS OF MORPHIA.—These salts are generally obtained by dissolving pure morphia in the dilute acids: they are colourless, and nearly all crystallizable, bitter, and are stated to give a precipitate of morphia with the alkaline carbonates, and with ammonia, but this is a doubtful character. Tannin, and infusion of galls, give precipitates with them, which are redissolved by acetic acid.

SULPHATE OF MORPHIA ($\text{Mor} + \text{S'}$) crystallizes in groups of acicular crystals, soluble in about twice their weight of water. This salt consists of

			Liebig.
Morphia	1	284	75·1
Sulphuric acid	1	40	10·6
Water	6	54	14·3
Crystallized sulphate of morphia	1	378	100·0

Dried at 250° this salt loses 4 atoms of water, but retains the 2 remaining atoms, (the quantity requisite to constitute crystallized morphia,)

till heated up to its decomposing point, so that that portion of water seems essential to the constitution of the sulphate.

BISULPHATE OF MORPHIA ($\text{Mor} + 2\text{S}'$) is obtained by dissolving the sulphate in excess of acid, and digesting in ether, which removes the excess of acid, but does not dissolve the bisulphate.

HYDROCHLORATE OF MORPHIA. ($\text{Mor} + \text{hc}'$).—This salt is formed in Gregory and Robertson's process above detailed: it may be produced directly by the action of hydrochloric gas upon morphia; it forms acicular and plumose crystals, soluble in about 20 parts of water, and when the hot solution cools, it concretes into a crystalline mass: this is the case when the salt is prepared by dissolving morphia in hot liquid hydrochloric acid. Hydrochlorate of morphia is an *anhydrous* salt, composed of

Morphia	1	284	88.47	Liebig. 88.7
Hydrochloric acid	1	37	11.53	11.3
Hydrochlorate of morphia	1	321	100.00	100.0

NITRATE OF MORPHIA ($\text{Mor} + \text{n}'$) is formed by dissolving morphia in very dilute nitric acid. It yields stellated groups of crystals, soluble in 1.5 of water.

PHOSPHATE OF MORPHIA ($\text{Mor} + \text{p}'$) crystallizes in cubes.

ACETATE OF MORPHIA ($\text{Mor} + \text{ac}'$) is frequently formed for medical use by dissolving a given weight of morphia in a sufficient quantity of distilled vinegar. It crystallizes difficultly in acicular bundles. During evaporation it easily parts with a portion of its acid, and is apt to be of uncertain composition; hence it is less appropriate for medical use than the hydrochlorate or sulphate.

2. CODEIA.—This alkaloid was discovered by Robiquet, in 1832, in the hydrochlorate of morphia prepared by Gregory and Robertson's process. (*Ann. de Ch. et Ph.*, li. 259.) On dissolving the mixed hydrochlorates in water, and precipitating the morphia by ammonia, the codeia remains, as already remarked, in solution, and crystallizes by subsequent evaporation: it may be separated, as above stated, by ether. According to Pelletier, 100 pounds of opium yield 6 ounces of codeia; according to Christison, the proportion of codeia varies in the varieties of opium, amounting in Turkey opium to one-thirtieth, and in East Indian opium to one-twelfth of the hydrochlorate of morphia obtained from those respective varieties.

Codeia crystallizes in acicular, or flat prisms, colourless, and transparent. It fuses without decomposition when heated in a tube to about 300° , and the mass crystallizes on cooling. In the air, it burns away with a smoky flame. Water, at 60° , dissolves 1.26 per cent.: at 110° , 3.7, and at 212° , 5.9 per cent. When it is present in larger proportions than the water can dissolve, the excess fuses, and remains at the bottom of the solution. Its solution is sensibly alkaline to tests. *Codeia* is soluble in the dilute acids, and forms distinct and easily crystallizable salts. Its medicinal action has not been accurately determined. It is distinguished from morphia by its greater solubility in water, by its insolubility

in fixed alkalis, by its not being reddened by nitric acid, nor blued by perchloride of iron.

Codeia is represented by $(31\text{ car} + 20\text{ h} + 50 + n)$, its equivalent being 260; or

						Robiquet.
Carbon	31	. .	186	. .	71.5 . . 72.0
Hydrogen	20	. .	20	. .	7.7 . . 7.5
Oxygen	5	. .	40	. .	15.4 . . 15.1
Nitrogen	1	. .	14	. .	5.4 . . 5.4
<hr/>						
Anhydrous codeia		1		260		100.0 . . 100.0

Crystallized codeia includes 2 atoms of water, its symbol therefore is $(\text{Cod} + 2\text{ q})$ and its equivalent 278 $(260 + 18)$. The only salt of codeia which has been analyzed, is the *hydrochlorate*; it is anhydrous, and consists of 260 codeia + 37 hydrochloric acid, its equivalent being 227, and its abbreviated symbol $(\text{Cod} + \text{hc})$.

3. NARCEIA.—This alkaloid, discovered by Pelletier in 1832, was obtained as follows. (*Ann. de Ch. et Ph.*, L. 262.) An infusion of Turkey opium was filtered and very carefully evaporated till it left a solid extract, which, redissolved in distilled water, left a large portion of crystallized narcotina; this being separated, the liquid was heated to 212° , and a slight excess of ammonia added to throw down morphia, after which the ebullition was continued for 10 minutes to drive off ammonia: on cooling the morphia crystallized, not pure, but mixed with narcotina and meconia. After having thus separated the greater part of the morphia by ammonia, the residuary liquor was reduced to half its original bulk by evaporation, and on cooling, morphia was again deposited, which being removed baryta water was added to the liquor, by which meconate of baryta was thrown down and separated by filtration. Subcarbonate of ammonia was then added to the filtered liquor to separate the remaining baryta, and heat applied to drive off the excess of the subcarbonate of ammonia. The liquor was then filtered, evaporated to the consistence of thick syrup, and left for several days in a cool place, when it formed a pulpy mass including crystals: this was suffered to drain, dried by strong pressure in linen, and digested in boiling alcohol; the alcoholic solution, reduced to a small bulk by distillation, furnished on cooling a crystalline substance: this, purified by repeated solutions and crystallization, is *narceia*.

Pure *narceia* forms white silky crystals, or acicular prisms, inodorous, bitterish and slightly pungent, soluble in 375 parts of cold and in 230 of boiling water; soluble in alcohol but not in ether; fusible at about 198° , and concreting into a white translucent and somewhat crystalline mass; it becomes yellow at 220° , and at higher temperatures is decomposed: it is more fusible than morphia or narcotina. It is decomposed by the stronger acids, but when diluted they dissolve and combine with it, producing at first a blue colour, which passes into purple or red, and then disappears. Narceia appears to consist of

						Pelletier.
Carbon	32	. .	192	. .	54.2 . . 54.73
Hydrogen	20	. .	20	. .	5.6 . . 6.52
Oxygen	16	. .	128	. .	36.2 . . 34.42
Nitrogen	1	. .	14	. .	4.0 . . 4.33
<hr/>						
Anhydrous narceia		1		354		100.0 . . 100.00

4. MECONIA.—This substance was discovered by Dublanc and Couerbe. (*Ann. de Ch. et Ph.*, L.) They obtained it by digesting opium in cold water, filtering the infusion, concentrating it by evaporation, and adding ammonia as long as it occasions a precipitate; after some days the supernatant liquid is poured off, gently evaporated to the consistence of syrup, and left in a cool place for 15 or 20 days, when it deposits granular crystals, which are collected, drained, pressed, and dried by a gentle heat: they contain meconia, narceia, and other substances: they are boiled in alcohol, and the solution is evaporated to about one-third its bulk, when on cooling it deposits crystals, which are collected, dissolved in boiling water, and filtered with animal charcoal: white crystals are obtained of meconia and narceia; ether dissolves the former and leaves the latter; on evaporating the ethereal solution the meconia remains. (This is only an outline of the essential parts of the process: the details of manipulation are omitted, but they will suggest themselves to the practical operator. The quantity of meconia in opium is so small, that from 15 to 20 lbs. must be operated upon satisfactorily to extract it.)

Meconia is white, inodorous, slightly acrid on the tongue, soluble in water, alcohol, and ether, and crystallizable; it fuses at 195° , and at about 350° it distils over unaltered, and concretes into a white mass looking like fat. It forms a colourless solution in sulphuric acid diluted with half its weight of water, but on applying heat to this solution it becomes green and is decomposed. Nitric acid dissolves it, and converts it into a peculiar crystallizable product. It is decomposed by chlorine.

The nature of this substance has been hitherto very imperfectly ascertained: according to Couerbe it contains no nitrogen, but consists of $(9\text{ car} + 4\text{ h} + 4\text{ o}) = 82$: or per cent. 60.23 carbon, 4.74 hydrogen, 35.03 oxygen.

5. THEBAIA. PARAMORPHIA.—This crystalline substance, discovered also by Couerbe, requires, like the former, further examination; it exists in opium in very small proportion, and can only be obtained, therefore, by those who have an opportunity of operating upon large quantities. Thebaia is represented as eminently alkaline, and as forming distinct salts by solution in the dilute acids. It is converted into a resinous product by the stronger acids, and is soluble in alcohol and ether. The formula of thebaia, according to Couerbe, is $(25\text{ car} + 14\text{ h} + 4\text{ o} + n)$, its equivalent being 210. Its crystals lose 2 atoms of water by fusion.

6. PSEUDOMORPHIA is a substance described by Pelletier as occasionally existing in opium; it resembles morphia in many of its properties, but is not poisonous; its formula is said to be $(27\text{ car} + 18\text{ h} + 3\text{ o} + n)$, its equivalent being 218.

7. NARCOTINA.—This well-defined and distinct principle was discovered in 1804 by Derosne. (*Ann. de Chim.*, xlv. 257.) Its peculiarities were first pointed out by Robiquet in 1817. (*Ann. de Ch. et Ph.*, v. and xi. 275.) Its alkaline characters are not very distinct, but the compounds which it forms with the acids, and its ultimate composition, place it among the alkaloids. It is contained in some kinds of opium, especially in that recently imported under the name of *Egyptian opium*, in a pro-

portion nearly, if not quite, equal to that of the morphia. The effects of this substance upon the animal economy have not been very satisfactorily ascertained, but there can be little doubt that they are perfectly distinct from those of morphia; opium, deprived of narcotina, is supposed to be more directly sedative, and less stimulating; hence the uses of the salts of morphia in preference to opium, and the advantage of using opium, in many instances at least, from which the narcotina has been abstracted.

Narcotina may be obtained from powdered opium by digesting it in warm ether, which takes up little else than narcotina, and yields it in crystals. When caustic potassa is added to an aqueous solution of opium, so as just to saturate the free acid, the matter which falls consists chiefly of resin and narcotina. When all the soluble parts of opium have been extracted by water, the residue, digested in dilute hydrochloric acid, also yields narcotina. Other means of obtaining narcotina and of separating it from morphia, will be evident, from the account of that alkaloid. Dr. Robertson's method consists in boiling the impure morphia in water, and adding sal-ammoniac, as long as ammonia is evolved in consequence of the decomposition of that salt by the morphia, at a boiling heat; the hydrochlorate of morphia so formed is dissolved, and the narcotina remains.

Narcotina is deposited from its alcoholic or ethereal solution in well-defined crystals, insoluble in cold and very sparingly soluble in hot water; soluble in the fat oils; not bitter; and yielding no blue colour with perchloride of iron: it is readily soluble in dilute acids, and yields salts which have been but imperfectly examined: they are very bitter, and difficultly obtained in the crystalline state, for when evaporated they are mostly decomposed into acid and narcotina, and crystals of the latter only separate. This is especially the case with the acetate of narcotina, and furnishes a means of separating it from morphia, for the latter substance is retained in permanent combination and solution. Narcotina absorbs hydrochloric acid gas, and is extremely soluble in hydrochloric acid, yielding a salt which is best obtained by carefully evaporating the hydrochloric solution of narcotina to dryness and redissolving in alcohol, from which solution the crystallized *hydrochlorate of narcotina* may be obtained: it consists, according to Robiquet of 91.1 narcotina + 8.9 hydrochloric acid. According to Liebig, the formula of narcotina is $(^{40}Car + ^{20}h + ^{12}o + n) = 370$, or

						Liebig.
Carbon	40	.	.	240	.	65.27
Hydrogen	20	.	.	20	.	5.32
Oxygen	12	.	.	96	.	25.63
Nitrogen	1	.	.	14	.	3.78
Narcotina	1			370	100.0	100.00

The following Table, drawn up by Mr. Pereira, gives the principal characters of the crystalline principles of opium (*Elements of Materia Medica*, 1284); but it is not stated from what authorities the formulæ and equivalents are derived.

TABULAR VIEW OF THE PRINCIPAL CHARACTERS OF THE CRYSTALLINE PRINCIPLES OF OPIUM.

Characters.	MORPHIA.	PSEUDO-MORPHIA.	CODEIA.	NARCOTINA.	THEBAINA.	NARCEINE.	MECONINE.
Taste	Very bitter ? ..	Bitter	{ Inspid; the salts bitter }	Rather acid and metallic	Slightly bitter ...	Rather acid.
Fusibility	Fusible	Infusible?	Fusible at 302° ..	{ Fusible at 338° }	Fusible at 266° ..	Fusible at 198° ..	Fusible at 194° ..
Ditto in Boiling Water	Infusible	Infusible	Fusible	{ .. }	Fusible	Fusible ..
Solubility in { Cold Water .. Boiling Water .. Cold Alcohol .. Boiling Alcohol .. Cold Ether .. Potash or Soda Ley	{ Insoluble, or nearly so ... }	Almost insoluble {	Soluble in 80 pts	Insoluble	Very slightly soluble	Soluble in 375 pts	Soluble in 266 pts
	Soluble in 100 pts	Less soluble than in water	Soluble in 17 pts	Soluble in 100 parts	Soluble in 10 pts	Soluble	Soluble in 19 pts.
	Ditto in 30 parts		Very soluble ..	Readily soluble	Still more soluble	More soluble	Soluble.
	Scarcely soluble				Very soluble	Insoluble	Soluble.
Basic quality { Action on Test Paper .. Satisfiability	Soluble	Soluble	Insoluble in the cold ley	Insoluble, or nearly so	Insoluble, unless the ley be very concentrated	Soluble.
	Alkaline ? ..	Alkaline	Neutral	Alkaline	Neutral	Neutral.
	Salifiable	Not salifiable ..	Salifiable	Salifiable	Salifiable?	Not salifiable ..	Not salifiable.
	Reddened: solution red	Reddened	Solution not red {	Made yellow: solution yellow	Gives it a resinous appearance, and dissolves it {	Coloured blue by dilute acid }	Solution yellow.
Coloured blue by Hydroch. Acid Not Not Not Not Not ..	Coloured blue Not.
Ditto by Sesquichloride of Iron ..	Coloured blue ..	Coloured blue Not Not Not Not Not.
Coloured blue by Iodine Not ? Not Not Not ..	Coloured blue Not.
Decomposes Iodic Acid	Decomposes Iodic acid ? Not Not Not Not Not.
Precipitated by Infusion of Nigalls	Precipitated ? ..	Precipitated	Precipitated ? Not Not.
When fused reddened by Chl. Gas Composition Not ? Not Not Not Not ..	Blood-red.
Equivalent	Cas H ₂₀ N ₁ O ₆ ..	C ₅₇ H ₁₈ N ₁ O ₁₄ ..	C ₃₅ H ₂₀ N ₁ O ₅ ..	C ₄₈ H ₂₄ N ₁ O ₁₅ ..	C ₂₅ H ₁₄ N ₁ O ₃ ..	C ₂₈ H ₂₀ N ₁ O ₁₂ ..	C ₁₀ H ₅ O ₄ ..
Water of Crystallization	292 ..	306 ..	284 ..	446 ..	202 ..	298 ..	97 (?) ..
Poisonous	Poisonous	Not poisonous ..	2 atoms ..	3 or 4 per cent. Inert?	1 atom ? ..	None. Inert?

8. MECONIC ACID.—The existence of a distinct acid in opium was announced by Seguin in 1804 (*Ann. de Ch.*, xcii. 225), and shortly afterwards by Sertuerner, who gave it the above name (from *μηκων*, poppy). (*Ann. de Ch. et Ph.*, v. 21.) It may be most conveniently extracted from the precipitate obtained by adding chloride of calcium to infusion of opium, in the process for procuring morphia (p. 1201). This precipitate is washed first with water, and then with hot alcohol, and mixed with 10 times its weight of water, at 195°, and hydrochloric acid is gradually added, so as to dissolve the *meconate of lime* (which forms the bulk of the precipitate) and leave the sulphate of lime; the solution is filtered, and on cooling deposits crystals of *bimeconate of lime*: these are again dissolved in hot dilute hydrochloric acid, by which the lime is abstracted, and crystals of meconic acid obtained, which, if pure, should leave no residue when burned: they must be redissolved in the acid, and recrystallized, till they are obtained in this state, but care must be taken to keep the temperature of their solutions below 212°. To abstract the whole of the colouring matter from this acid, it must be saturated by a weak solution of caustic potassa, and the meconate of potassa dissolved by the aid of gentle heat in a little water: when cold, the fluid part, which retains the colour, must be pressed out of the crystals, and these, decomposed as before by hydrochloric acid, ultimately yield the meconic acid in small white crystals, which must be dried at a temperature below 100°.

Meconic acid crystallizes in transparent and micaceous scales of an acid taste, soluble in 4 parts of hot water, and in alcohol. The crystals are permanent in the air, but when heated to 212° they lose 21·5 per cent. of water: they then sustain a temperature of 240° without decomposition; but if boiled in water, carbonic acid is evolved, the solution becomes brown, and *metameconic acid* is formed.

Meconic acid consists, according to Liebig (*Ann. de Ch.*, liv. 26), of ($7\text{ car} + 2\text{ h} + 7\text{ o}$), its equivalent being = 100, or

	Liebig.		
Carbon . . .	7	42	42·46
Hydrogen . . .	2	2	1·98
Oxygen . . .	7	56	55·56
Meconic acid	1	100	100·00

MECONATES.—The meconic acid forms neutral, acid, and sub-salts: the bimeconates are difficult of decomposition. One of the leading characters of this acid and of its salts, is that of forming compounds with the peroxide of iron of an intensely red colour, very similar to that of the sulphocyanate of iron; so that the persalts of iron are excellent tests of its presence, and by them opium may sometimes be recognised, where the quantity is so small as to render the morphia very difficult of detection. This red colour is destroyed by heat, and by sulphurous acid and protochloride of tin; but it returns on exposure to air, or on the addition of a few drops of nitric acid. A few drops of laudanum or other compound of meconic acid in 6 or 8 ounces of distilled water, to which 2 or 3 drops of solution of potassa have been added, is blackened on the addition of a few drops of solution of gold in nitrohydrochloric acid; the effect takes place in a few minutes, when the solutions are even more dilute. Mr. J.

T. Cooper uses this test as distinctive between the meconic acid and the sulphocyanic and indigotic acids, all of which redden the persalts of iron, but the former only blackens the potassachloride of gold.

The meconates of ammonia and of potassa become less soluble by excess of acid; the meconates of lime, baryta, strontia, and lead, are rendered more soluble by excess of acid; when neutral, they are insoluble, or nearly so, in water; but soluble in nitric acid. The meconate of lead may be decomposed by sulphuretted hydrogen. The *meconate of silver* ($\text{Ag} + \text{mec}'$) is thrown down in the form of a white powder, when nitrate of silver is dropped into a solution of meconic acid: if the precipitate be redissolved by the addition of nitric acid, and the mixture heated, *cyanuret of silver* is produced: the liquid originally transparent, becomes opaque from the formation of the cyanuret, and when this is deposited, *oxalate* of silver is found in the supernatant liquid, which may be thrown down by the cautious addition of ammonia; excess of nitric acid converts the whole into oxalate, without any formation of cyanuret. (LIEBIG.)

8. METAMECONIC ACID.—When an aqueous solution of meconic acid is boiled, it is converted into metameconic acid and carbonic acid: the acid at the same time becomes discoloured; so that pure and colourless metameconic acid is best obtained by decomposing meconate of potassa or of lime, at a *boiling heat*, by hydrochloric acid; it is then less coloured, and may be obtained colourless by the help of animal charcoal.

Metameconic acid is less soluble than the meconic; it forms hard crystalline grains, requiring 16 parts of hot water for solution. It reddens the persalts of iron; and is converted into oxalic acid by nitric acid. The neutral metameconates of ammonia and potassa are difficultly soluble in water: excess of acid renders them more soluble.

Metameconic acid is anhydrous, and consists, according to Liebig, of ($^{12}\text{car} + 4\text{h} + ^{10}\text{o}$), its equivalent being 156, or

					Liebig.
Carbon	12	. .	72	. .	46.1 . . 46.62
Hydrogen	4	. .	4	. .	2.6 . . 2.53
Oxygen	10	. .	80	. .	51.3 . . 50.85
Anhydrous metameconic acid	1		156		100.0 . . 100.00

Hence 2 atoms of meconic acid $= 2(^7\text{car} + ^2\text{h} + ^7\text{o})$, yield 1 atom of metameconic acid $= (^{12}\text{car} + 4\text{h} + ^{10}\text{o})$, and 2 atoms of carbonic acid $= 2(\text{car} + ^2\text{o})$, and this represents the change which the meconic acid suffers when boiled with water.

9. PYROMECONIC ACID.—This acid is among the products of the destructive distillation of the meconic acid; it is a crystalline sublimate, which fuses at a temperature of about 250° . It is volatile, soluble in water and alcohol, reddens the persalts of iron, and forms many soluble salts. This acid, when anhydrous, appears to be constituted of ($^{10}\text{car} + 3\text{h} + ^5\text{o}$) = 103. The neutral pyromeconate of lead consists of

					Liebig.
Pyromeconic acid	1	. .	103	. .	47.9 . . 48.3
Oxide of lead	1	. .	112	. .	52.1 . . 51.7
Anhydrous pyromeconate of lead	1		215		100.0 . . 100.0

Dumas observes, that the *hydrated* pyromeconic acid, consisting of 1 atom of the anhydrous acid and 1 of water, is isomeric with the anhydrous pyrocitric, and with the hydrated pyromucic acid.

II. CINCHONIA. QUINIA. ARICINA. CINCHONIC ACID.—The existence of a peculiar principle in *pale Peruvian bark*, (the bark of the *Cinchona Condaminea* or *lancifolia*), was originally suggested by the late Dr. Duncan; he considered it as the source of its medicinal powers, and proposed to call it *Cinchonine*; it was afterwards procured in a crystalline form by Dr. Gomès of Lisbon; but its peculiar alkaloid properties, and ready and certain methods of preparing it, were first made known by Pelletier and Caventou, in 1820. (*Ann de Ch. et Ph.*, xv. 291 and 337.) They also discovered another analogous but distinct principle in *Yellow Peruvian Bark* (*Cinchona cordifolia*), which has been termed *Quinia*; and in the *Red Peruvian Bark* (*Cinchona oblongifolia*), they found the two preceding alkaloids, nearly in equal proportions. In 1829, Pelletier and Coriol discovered a third alkaloid in a species of bark from Arica, the botanical history of which is not known, but which they have termed *Aricina**.

1. CINCHONIA.—This alkaloid may be obtained from pale Peruvian bark† by the following process. A pound of the bruised bark (*Cinchona lancifolia* of the Pharmacopœia) is boiled in about a gallon of water, acidulated by 3 fluid drachms of sulphuric acid. A similar decoction is repeated with about half the quantity of liquid, and so on, till all the soluble matter is extracted. The decoctions are then mixed and strained, and powdered lime added, in a proportion somewhat greater than necessary to saturate the acid: the precipitate that ensues (a mixture chiefly of cinchonia and sulphate of lime) is collected, *carefully* dried, and boiled for some minutes in strong alcohol, which is then decanted off, while hot and fresh portions are successively added for the repetition of the same operation, until it ceases to act upon the residue, which is now little else than sulphate of lime. The different alcoholic solutions are then put into a retort or still, and considerably evaporated; during which, and especially on cooling, cinchonia is deposited. When the whole is thus collected, the cinchonia must be redissolved in alcohol, and crystallized by its slow evaporation. It may be deprived of colour and slight impurities by the action of animal charcoal, and two or more crystallizations. In the preceding process hydrochloric acid may be used instead of sulphuric, in which case the precipitate is not encumbered with sulphate of lime.

Cinchonia is thus obtained in the form of white semitransparent crystals, requiring about 2500 parts of water, at 212°, for their solution, and are almost insoluble in cold water. They have little taste, but become intensely bitter upon the addition of almost any acid. They

* The French chemists designate these bases by the termination *ine*, morphine, quinine, &c. As far as possible we are in the habit of distinguishing *salifiable bases* by the termination *a*, hence our terms *morphia*, *quinia*, *cinchonia*, &c.

† The varieties of Peruvian bark have been examined by MM. Pelletier and

Caventou. In the *Cinchona lancifolia*, or *pale bark*, they found the following constituent parts:—1. Cinchonia, combined with kinic (or cinchonic) acid. 2. Green fatty matter. 3. Red and yellow colouring matter. 4. Tannin. 5. Kinate (or cinchonate) of lime. 6. Gum. 7. Starch. 8. Lignin.

restore the blue colour of reddened litmus. They are sparingly soluble in cold alcohol, ether, and fixed oils; but abundantly soluble in boiling alcohol, and the solution deposits crystals on cooling, and becomes milky when dropped into water.

When cinchonia is heated in a small tube-retort, ammonia is evolved, recognised by its odour, action upon turmeric, and upon a glass rod moistened with hydrochloric acid; the odour of hydrocyanic acid may also be perceived; an oily matter, smelling like naphtha, distils over, and an abundant carbonaceous residue remains. The most remarkable circumstance attending this decomposition (provided the cinchonia be pure, and air carefully excluded), is the absence of aqueous vapour, even when the products were made to pass through a cooled tube. This led me to suspect the absence of oxygen in cinchonia (*Quarterly Journal*, xvi.); an opinion corroborated by its want of action upon potassium when heated with that metal in naphtha: the cinchonia, under these circumstances, readily dissolves in boiling naphtha, and again entirely separates as the solution cools, concreting into a radiated crystallized mass, in which the brilliant globules of potassium are disseminated. The experiments which I made to determine the ultimate components of cinchonia, led me to regard it as a ternary compound of 79.3 per cent. carbon, 7.1 hydrogen, and 13.6 nitrogen, and I represented it as a *base*, of which certain other alkaloids might possibly be *oxides*; but the subsequent, and probably more accurate researches of Pelletier and Dumas have shown that it consists of ($^{20}car + ^{12}h + o + n$), its apparent equivalent being 154; or

				Dumas and Pelletier.		Brande.
Carbon .	20	. . . 120	. . . 78.4	. . . 78.67	. . . 79.3	
Hydrogen	12	. . . 12	. . . 7.2	. . . 7.06	. . . 7.1	
Oxygen .	1	. . . 8	. . . 5.2	. . . 5.16	. . . 0.0	
Nitrogen	1	. . . 14	. . . 9.2	. . . 9.11	. . . 13.6	
Cinchonia	1	154	100.0	100.00	100.0	

The salts of cinchonia have been examined by Baup (*Ann. de Ch. et Ph.*, xxvii. 323), and by Pelletier, Caventou, and Dumas. (*Ann. de Ch. et Ph.*, xv. and xxiv.)

SULPHATE OF CINCHONIA.—There is a *subsulphate* or disulphate, and a neutral sulphate of this base. The *neutral sulphate*, obtained by dissolving cinchonia in excess of dilute sulphuric acid, and evaporating till a pellicle forms, crystallizes in rhomboidal octoëdra, which become opaque, and are efflorescent, soluble in less than their weight of water at 60°, and in alcohol, but not in ether. They consist of ($Cin + S' + 4q$), or

				Baup.
Cinchonia	1	. . . 154	. . . 67.0	. . . 67.241
Sulphuric acid	1	. . . 40	. . . 17.4	. . . 17.241
Water	4	. . . 36	. . . 15.6	. . . 15.518
Crystallized sulphate of cinchonia	1	230	100.0	100.000

SUBSULPHATE, OR DISULPHATE OF CINCHONIA.—This salt requires between 50 and 60 parts of water at 60° for its solution: it is obtained by digesting excess of cinchonia in the dilute acid: it forms rhomboidal prisms = ($2Cin + S' + 2q$), or composed of

Cinchonia	2	308	Baup. 84.41
Sulphuric acid	1	40	10.91
Water	2	18	4.68
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Crystallized disulphate of cinchonia	1	366	100.00

HYDROCHLORATE OF CINCHONIA. ($\text{Cin} + \text{HCl}$).—Anhydrous cinchonia absorbs hydrochloric acid gas, and produces a neutral hydrochlorate, composed, according to Liebig, of

Cinchonia	1	154	80.6	Liebig. 81
Hydrochloric acid	1	37	19.4	19
<hr/>				
Hydrochlorate of cinchonia	1	191	100.0	100

DIHYDROCHLORATE OF CINCHONIA. ($2\text{Cin} + \text{HCl}$).—When cinchonia in excess is digested in dilute hydrochloric acid, a soluble salt, forming acicular crystals, is obtained, composed, according to Pelletier and Caventou, of

Cinchonia	2	308	89.3	Pelletier. and Caventou. 89.5
Hydrochloric acid	1	37	10.7	10.5
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Dihydrochlorate of cinchonia	1	345	100.0	100.0

NITRATE OF CINCHONIA. ($\text{Cin} + \text{HNO}_3$).—When very dilute nitric acid is saturated by cinchonia, a portion of the *nitrate* formed separates in the form of liquid globules, looking like oil, which, in the course of a few days, become groups of acicular crystals. This property belongs also to quinia, and may serve to distinguish these from other alkaloids.

CHLORATE OF CINCHONIA, ($\text{Cin} + \text{ClO}_3$), obtained by saturating chloric acid by cinchonia, forms clusters of white crystals. When heated, they first fuse and then explode.

IODATE OF CINCHONIA forms delicate prismatic crystals.

ARSENATE OF CINCHONIA is a very soluble, and difficultly-crystallizable salt.

GALLATE OF CINCHONIA is a difficultly-soluble salt.

OXALATE OF CINCHONIA.—The neutral oxalate is difficultly soluble in cold water: it is rendered more soluble by excess of acid; it is thrown down when oxalate of ammonia is added to a neutral solution of a salt of cinchonia, in the form of a white powder, very sparingly soluble in hot water: this salt is soluble in hot alcohol, and part separates as the solution cools.

ACETATE OF CINCHONIA.—Acetic acid dissolves cinchonia: the solution is always acid; when evaporated it lets fall small crystals on cooling, which are neutral and difficultly soluble. When, on the contrary, the solution is evaporated to dryness, a gum-like mass is obtained, which is resolved by cold water into a soluble superacetate, and an insoluble subacetate.

CARBONATE OF CINCHONIA.—This salt is said to be precipitated from the solutions of cinchonia by carbonated alkalis, and moist cinchonia is stated to absorb carbonic acid from the air, and then to effervesce when dissolved in acids.

2. QUINIA.—Quinia is obtained from *yellow bark* by a process precisely similar to that for procuring cinchonia from pale bark. But, as sulphate of quinia is abundantly prepared for medical use, that salt is a more ready source of the alkaloid: it is obtained by adding ammonia to a solution of the sulphate, when it falls in white flakes, which are apt, on drying, to become brown. Quinia is very difficult of crystallization, but it has been obtained in that form by very slowly evaporating its alcoholic solution by exposure to cold dry air. It may also be crystallized, according to Henri and Delondre (*Jour. de Pharm.*, xx. 157), by dissolving pure and crystallized sulphate of quinia in a large quantity of water, decomposing it by ammonia, washing the precipitate, dissolving it in weak alcohol, and adding water to the solution till it becomes milky: it is then left for some days exposed to the air, when portions of the separated quinia, which at first resembled fluid resin, gradually become crystalline, forming radiated and acicular groups, which are efflorescent. These crystals are *hydrate of quinia*; when heated they first soften, then become white and pulverulent, and, when fused, lose water; the fused quinia concretes into a resin-like mass, which, if cooled very slowly, shows signs of crystallization, and becomes negatively electric by friction: in water it gradually returns to the state of hydrate.

Quinia has a decided alkaline action upon proper tests; it is intensely bitter; very sparingly soluble, even in boiling water; readily soluble in boiling alcohol, which, when evaporated, leaves it in the form of a viscid mass: it is more soluble than cinchonia in ether. It forms distinct salts with the acids*. When heated in a tube it fuses, becomes thick, viscid, and dark-coloured, an oily liquid evaporates, ammoniacal and hydrocyanic vapours follow, and a bulky carbonaceous matter remains.

Anhydrous quinia consists of $(20 \text{ car} + 12 \text{ h} + 2 \text{ o} + \text{n}) = 162$; or,

				Pelletier and Liebig.	Göbel.	Brandé†.
Carbon	2	120	74.1	74.39	72.28	73.80
Hydrogen	1	12	7.4	7.25	8.33	7.65
Oxygen		16	9.9	9.74	11.10	5.55
Nitrogen	1	14	8.6	8.62	8.29	13.00
Anhydrous quinia	1	162	100.0	100.00	100.00	100.00

* When quinia is obtained from the common varieties of yellow bark, it almost always contains more or less cinchonia: these alkaloids may be separated by solution in alcohol, which, when duly evaporated, deposits the cinchonia in crystals, while the quinia, being more soluble, remains in solution: by one or more repetitions of this process it may be freed from cinchonia: or they may be converted into *sulphates*, and then, the sulphate of quinia, being less soluble than the sulphate of cinchonia, crys-

tallizes, and leaves the latter salt in solution.

† I insert my own analyses here, because they were made with much care at the time, and are consistent with the results of Pelletier, Dumas, and Liebig, as far as the carbon and hydrogen are concerned; in respect to the nitrogen, I cannot account for the discrepancy, or for the cause of the probable error in my own experiments. These analyses, which were published in the *Quarterly Journal*, vol. xvi., formed part of a paper which

SULPHATE OF QUINIA.—This salt has excited great attention on account of its medicinal importance; its manufacture is chiefly carried on in Paris*, though large quantities of it have occasionally been prepared in this country. The quinia is obtained from yellow bark, and dissolved in dilute sulphuric acid: the first crops of the salt are decoloured by animal charcoal; it is again crystallized, and very carefully dried: this operation requires care, for if the desiccation is carried too far, the salt loses its crystalline character, and crumbles down into powder.

The *sulphate of quinia*, as it occurs in commerce, is at present regarded as a subsalt, or a **DISULPHATE**, and is such, in reference to the above equivalent of quinia; but by some, an equivalent has been assumed which represents this as a neutral sulphate.

DISULPHATE OF QUINIA forms long acicular crystals, efflorescent, intensely bitter, and requiring about 740 parts of cold, and 30 parts of boiling water, for their solution. They are soluble in 24 parts of cold alcohol (specific gravity 850), and much more soluble in boiling alcohol. This salt readily fuses, looking at first like melted wax; it then reddens, and begins to be decomposed; in the air it burns, producing at first a bulky charcoal, which, by continued heat, is consumed without residue: we are thus enabled to discover certain adulterations which are practised upon it†. It has the curious property of becoming luminous when heated to about 212°; its phosphorescence is increased by friction, and electricity is, at the same time, manifest.

The accurate determination of the composition of this salt, in its various states, is interesting and important; upon this subject there is some difference in the statements of different authors: the following, as given by Dumas and Baup, agrees with my own observations, but Liebig does not admit the existence of an anhydrous basic sulphate, which ought to consist of

was intended for the Royal Society, and in which I first pointed out the existence of nitrogen as a characteristic element of the alkaloids then known. The paper was not read, and on the arrival of the *Annales de Chimie*, containing Pelletier and Dumas' announcement of the same fact, it was withdrawn at the recommendation of the President.

* 120,000 ounces are annually exported from Paris. (DUMAS.)

† The substances commonly employed for the adulteration of sulphate of quinia are, water, sugar, gum, starch, ammoniacal salts, and earthy salts, such as sulphate of lime and magnesia, or acetate of lime. Pure sulphate of quinia, when deprived of its water of crystallization by a heat of 212°, should lose only from 8 to 10 per cent. of water. Sugar may be detected by dissolving the suspected salt in water, and adding precisely so much carbonate of potassa as will pre-

cipitate the quinia. The taste of the sugar, no longer obscured by the bitter of the quinia, will generally be perceived; and it may be separated from the sulphate of potassa by evaporating gently to dryness and dissolving the sugar by boiling alcohol. Gum and starch are left when the impure sulphate of quinia is digested in strong alcohol. Ammoniacal salts are discovered by the strong odour of ammonia, which may be observed when the sulphate is put into a warm solution of potassa. Earthy salts may be detected by burning a portion of the sulphate. Several of the preceding directions are taken from a paper on the subject by Mr. Phillips. (*Phil. Mag. and Ann.*, iii. 111, and *TURNER'S Elements*.)

According to Dumas, *margaric acid* is sometimes mixed with sulphate of quinia; it is detected by its insolubility in dilute hydrochloric acid.

Quinia	2	324	89	Baup. 89.1
Sulphuric acid	1	40	11	10.9
Anhydrous disulphate of quinia	1	364	100	100.0

The ordinary sulphate of quinia, or the *crystallized disulphate*, consists of

Quinia	2	324	74.3	Dumas. 74.6
Sulphuric acid	1	40	9.2	9.1
Water	8	72	16.5	16.3
Crystallized disulphate of quinia	1	436	100.0	100.0

When the salt effloresces, or when dried at 212° , it loses 4 atoms of its water, and when dried at 240° it loses 6 atoms, retaining 2, which, according to Baup, may be expelled by a higher temperature, but which are retained, according to Liebig, till the salt decomposes.

When the *disulphate of quinia* is triturated with dilute sulphuric acid, it first forms a white magma, which afterwards dissolves on adding more of the acid, and on evaporating this solution, or, if concentrated, on leaving it at rest, prismatic crystals of the *neutral sulphate* (according to our equivalent) are formed. This salt is much more soluble than the preceding, and at 212° it fuses in its water of crystallization; when dissolved in alcohol its solution yields crystals, which fall to powder on exposure to air. This sulphate, in crystals, is composed, according to Dumas, of

Quinia	1	162	59.1	Dumas. 59.4
Sulphuric acid	1	40	14.6	14.3
Water	8	72	26.3	26.3
Crystallized sulphate of quinia	1	274	100.0	100.0

The various sulphates of quinia, therefore, may be thus represented:

	Symbols.	Equivalents.
1. Anhydrous disulphate . . .	$= (2 \text{ QUI} + \text{S}') . . .$	364
2. Crystallized disulphate . . .	$= (2 \text{ QUI} + \text{S}' + 8 \text{ q}) . . .$	436
3. Effloresced disulphate . . .	$= (2 \text{ QUI} + \text{S}' + 4 \text{ q}) . . .$	400
4. Ditto, dried at 240° . . .	$= (2 \text{ QUI} + \text{S}' + 2 \text{ q}) . . .$	382
5. Anhydrous sulphate . . .	$= (\text{ QUI} + \text{S}') . . .$	202
6. Crystallized sulphate . . .	$= (\text{ QUI} + \text{S}' + 8 \text{ q}) . . .$	274

HYDROCHLORATE OF QUINIA. ($\text{QUI} + \text{hc}'$).—When dry quinia is exposed to a current of hydrochloric acid gas, it absorbs 18 per cent., and forms a salt more soluble than the sulphate. (LIEBIG.) When quinia is dissolved in hydrochloric acid, the solution affords nacreous crystals on evaporation, which are more soluble than sulphate of quinia, and less soluble than hydrochlorate of cinchonia; they contain about 7 per cent. of hydrochloric acid. (PELLETIER and CAVENTOU.) Probably, therefore, there are two hydrochlorates of quinia: regarding Liebig's salt as *anhydrous*, it would consist of

Quinia	1	162	81.4	Liebig. 81.9
Hydrochloric acid	1	37	18.6	18.1
Anhydrous hydrochlorate of quinia	1	199	100.0	100.0

NITRATE OF QUINIA.—When quinia is dissolved in diluted nitric acid, and the solution evaporated, the nitrate separates in the form of an oil-like liquid, which gradually crystallizes. (PELLETIER. CAVENTOU. DUMAS.)

PHOSPHATE OF QUINIA is easily crystallizable; it forms acicular prisms, soluble in alcohol. (PELLETIER and CAVENTOU.)

CHLORATE OF QUINIA, formed by dissolving quinia in chloric acid, yields, on evaporation, bundles of acicular prisms, which, when heated, fuse, and afterwards explode. (DUMAS.)

IODATE OF QUINIA forms silky crystals. (DUMAS.)

ARSENATE OF QUINIA much resembles the appearance of the phosphate, but its crystals are less nacreous. (PELLETIER and CAVENTOU.)

OXALATE OF QUINIA.—When a concentrated solution of oxalic acid is added to one of a soluble salt of quinia, a precipitate of oxalate of quinia falls; it dissolves in boiling water, and yields nacreous acicular crystals on cooling; it dissolves in excess of oxalic acid, and this solution also crystallizes in needles: the neutral oxalate is very soluble in alcohol, and the hot alcoholic solution deposits crystals on cooling.

TARTRATE OF QUINIA resembles the oxalate, but is more soluble.

TANNATE OF QUINIA.—The infusion and tincture of galls precipitates quinia from its solutions: pure tannic acid produces a similar effect: the precipitate is soluble in acetic acid, and difficultly so in water.

GALLATE OF QUINIA.—Gallic acid occasions precipitates in all the solutions of quinia which are not very dilute; the alkaline gallates are yet more effective precipitants. Gallic acid unites directly with quinia, and the salt is difficultly soluble in cold water; its solution in boiling water becomes milky as it cools. The gallate of quinia is soluble in alcohol, and in excess of acid. (DUMAS.)

ACETATE OF QUINIA.—The acetate of quinia, when slightly acid, is easily crystallizable: the solution, when evaporated to a certain point, forms a mass of distinct acicular crystals; when very slowly evaporated, it yields peculiar mamillary and stellated groups; it is not very soluble, and if coloured, it may be washed in water, and subsides in silky filamentous crystals: its concentrated solution, in boiling water, concretes into a crystalline mass when cold. (DUMAS.)

Mr. Pereira has given the following comparative table of the principal distinctive characters of cinchonia and quinia. (*Elements of Materia Medica*, p. 997.)

		CINCHONIA.	QUINIA.
Form		Crystalline.	Amorphous (in the anhydrous state). The hydrate is crystallizable, but with difficulty.
Taste.....		Bitter.	Very bitter.
Fusibility.....		Infusible when quite dry; when moist fuses, but at the same time decomposes.	Fusible.
Composition		1 atom contains only 1 atom of oxygen.	1 atom contains 2 atoms of oxygen.
Combining proportion, or atomic weight.....		154	162
Solubility	in water.....	Dissolves in 2500 times its weight of boiling water	Dissolves in 200 times its weight of boiling water.
	in alcohol.....	Soluble; solution readily crystallizes.	More soluble than cinchonia; solution with difficulty crystallizes.
	in ether.....	Sparsingly soluble; solution readily crystallizes.	Very soluble; solution crystallizes with difficulty.
Salts.	Disulphate { form and aspect..... solubility.....	Four-sided prisms. Soluble in 54 parts of cold water or 6 parts of spirit (sp. gr. 0·85).	Pearly silky needles. Soluble in 740 parts of cold water or 80 parts of spirit (sp. gr. 0·85).
	Neutral Sulphate	Soluble in half its weight of cold water or 1 part of cold spirit (sp. gr. 0·85).	Soluble in 11 parts of cold water. More soluble in spirit than sulphate of cinchonia.
	Hydrochlorate	Crystallizes in needles.	Crystallizes in silky or pearly tufts.
	Phosphate	Scarcely crystallizable; aspect gummy.	Crystallizes in pearly needles.
	Arseniate	Scarcely crystallizable.	Crystallizes in prismatic needles.
	Acetate	Very soluble; crystals small and granular.	Less soluble; crystals in silky tufts, grouped in stars, &c.
The solution of disulphate treated by chlorine, then by ammonia, yields		A reddish solution.	An emerald-green solution.

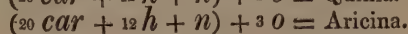
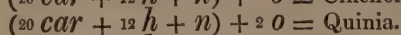
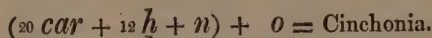
3. ARICINA.—This alkaloid was discovered in 1829, by Pelletier and Coriol, (*Jour. de Pharm.*, xv. 575,) in a bark from Arica, which had been fraudulently mixed with cinchona: in appearance it resembles *yellow bark*, but we are unacquainted with its botanical history. Treated as usual for the separation of its alkaloid, it yields a substance much resembling cinchonia in its external characters, but differing from it materially in its aggregate chemical properties. It is insoluble in water, and nearly tasteless, but, after a time, produces a biting sensation upon the palate; its acid solutions are very bitter; heated, it fuses like quinia, and is not volatile.

Its *sulphate* is not crystallizable from its aqueous solution, but yields a gelatinous mass, becoming horny when dried: its alcoholic solution, on the contrary, affords silky crystals, much like sulphate of quinia. When a few drops of sulphuric acid are added to its gelatinous sulphate, another sulphate, crystallizable in flattened prisms, is formed. The action of nitric acid on *aricina* is very distinct; when concentrated it produces with it a very deep green colour; when more dilute the colour is brighter, and when very dilute the solution is colourless: the production of this green colour is accompanied by a decomposition of the alkaloid, but, by using a

very dilute acid for its solution, this is prevented, and a colourless nitrate obtained. According to Pelletier, the ultimate components of aricina are

				Pelletier.
Carbon	20	. .	120	. . 70·6
Hydrogen	12	. .	12	. . 7·1
Oxygen	3	. .	24	. . 14·1
Nitrogen	1	. .	14	. . 8·2
Aricina	1		170	100·0
				100·0

It is remarked by Dumas, that cinchonia, quinia, and aricina, may be regarded as oxides of a common radical or base, represented as follows:—



The atomic constitution of these, and of the preceding alkaloids, suggests many theoretical views, which, however, have not been sufficiently matured to merit a place here, and are essentially dependent upon the equivalents by which they are represented. The numbers which I have adopted represent these bodies as *nitrurets* of a compound radical, or as consisting of carbon, hydrogen, and oxygen + 1 atom of nitrogen; hence the notion of the existence in them of ammonia, to which, even their alkaline characters have been by some ascribed: Dumas compares them to urea, and regards them as amides; but these hypotheses are all unsatisfactory, and till our knowledge of the various hydrocarbons, and of their combinations, is much extended and simplified, we shall probably not be able to frame any correct theory applicable to the ultimate constitution of these highly interesting compounds.

4. CINCHONIC (KINIC) ACID.—This acid, originally noticed by Hofmann, and by Vauquelin (*Ann. de Ch.*, Lix. 162), is contained in the different species of *cinchona*, combined with lime, and with their alkaloids. It may be obtained by digesting an aqueous extract of cinchona in alcohol, which leaves a viscid mass containing cinchonate of lime: when this is dissolved in water, and exposed to spontaneous evaporation in a warm place, the salt of lime crystallizes, and these crystals, when purified, may be decomposed by sulphuric or oxalic acid, so as to abstract the lime, and separate the cinchonic acid; some add acetate of lead to the solution of cinchonate of lime, and decompose the precipitated cinchonate of lead by sulphuretted hydrogen, but the former methods are preferable. (HENRY and PLISSON, *Jour. de Pharm.*, xiii. and xv.; LIEBIG and BAUP, *Ann. de Ch. et Ph.*, xlvii. 188, and Li. 56.) When the cinchonic acid is separated its aqueous solution must be slowly and quietly evaporated, and it then yields crystals, soluble in 2·5 of water at 68°, and soluble also in alcohol: it tastes sour, but not in the least bitter. Sulphuric acid dissolves it, acquiring a green colour, and carbonizes it when heated. Heated with a little nitric acid, a crystallizable sublimate is at first produced, which is analogous to *pyrocinchonic acid*; a larger addition of the acid converts it into oxalic acid. According to Baup, the formula of this acid is ($car + ^{10} h + ^{10} o$), so that its equivalent is 180, or

				Baup.	Liebig.
Carbon	15 . . . 90 . . .	50.0 . . .	50.0 . . .	46.23	
Hydrogen	10 . . . 10 . . .	5.5 . . .	5.6 . . .	5.89	
Oxygen	10 . . . 80 . . .	44.5 . . .	44.4 . . .	47.88	
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Anhydrous cinchonic acid	1 . . . 180 . . .	100.0 . . .	100.0 . . .	100.00	

The crystallized cinchonic acid includes 1 atom of water, its equivalent being $180 + 9 = 189$.

CINCHONATES OR KINATES.—In the *neutral cinchonates*, the oxygen in the acid is to that in the base as 10 to 1. They are soluble in water, but insoluble in absolute alcohol.

CINCHONATE OF LIME. ($C + cin'$).—This salt crystallizes in transparent rhomboids, soluble in 9 parts of water at 60° , and much more soluble in hot water: when dried at 212° it loses 28 per cent. of water. Its equivalent in the *anhydrous* state is $180 + 28 = 208$, and in the *crystallized* state, including 10 equivalents of water, $208 + 90 = 298$. According to Berzelius, a small quantity of cinchonate of lime may be extracted from the alburnum of fir-trees.

CINCHONATE OF COPPER ($Cu + cin'$) is thrown down in the form of a difficultly-soluble green precipitate, when a soluble cinchonate is added to a solution of acetate of copper; the salt is not thrown down from sulphate or nitrate of copper. According to Baup, this is a basic salt.

CINCHONATE OF LEAD. ($Pb + cin'$).—The *neutral* salt forms acicular crystals, which, when gently heated, lose their water of crystallization. The *basic* salt is insoluble in water.

CINCHONATE OF SILVER ($Ag + cin'$) is an anhydrous salt, which rapidly blackens by exposure to light.

III. STRYCHNIA. BRUCIA. STRYCHNIC ACID.—Strychnia was discovered in 1818, by Pelletier and Caventou. (*Ann. de Ch. et Ph.*, viii. 305, x. 142.) It is contained in many species of *Strychnos*, especially in *S. nux-vomica*, *S. ignatia*, and *S. colubrina*. They also subsequently detected it in the celebrated Javanese poison, called *Upastieule*. (*Ann. de Ch. et Ph.*, xxvi. 44.) Strychnia is associated in the former sources with *Brucia*, a distinct alkaloid, which was originally detected in the bark of the *nux-vomica* tree, an article which was known in the drug-trade under the name of *spurious angustura bark*; and as the genuine *angustura bark* was presumed to be the bark of a species of *brucia*, the terms *brucine* and *brucia*, though evidently derived from a perfectly distinct source, have been applied to the alkaloid extracted, together with strychnia, from the bark of the *S. nux-vomica*. *Brucia* was discovered by the above chemists in 1819. (*Ann. de Ch. et Ph.*, xii. 118.) To them also we are indebted for our knowledge of the *strychnic*, or as they originally called it, *igasuric* acid, a term derived from the Malayan name of St. Ignatius' bean.

1. STRYCHNIA.—Among the numerous processes which have been devised for the extraction of strychnia, the two following are the

simplest: the first is suggested by M. Coriol, the second by M. Henry, jun. (*Jour. de Pharm.*, xi. 492, xvi. 752.)

Digest coarsely-powdered *nux-vomica* in repeated portions of cold water, till all soluble matters are extracted: carefully evaporate the infusions to the consistence of syrup, and precipitate by alcohol; wash the precipitate (which consists of gum) with alcohol, add the washings to the original portion, and evaporate the whole in a water bath to the consistency of an extract: this consists almost entirely of strychnate of strychnia; dissolve it in cold water, which separates a little greasy matter; then heat the clear liquid, and add milk of lime so as to decompose the strychnate, and leave the lime in slight excess; drain, and dry the precipitate by pressure, and digest in boiling alcohol, which takes up strychnia, brucia, and some colouring matter; these are obtained by evaporation, and may be separated by the action of weak alcohol, which dissolves the brucia and the colouring matter, and leaves strychnia; wash it with a little dilute alcohol, and dissolve it in strong boiling alcohol; this deposits it in crystals on cooling.

Henry's process is as follows: the rasped or powdered *nux-vomica* is digested in warm alcohol acidulated by sulphuric acid, as long as it dissolves anything; it is then pressed out, and powdered quick-lime is added to the alcoholic liquors to saturate the acid, and precipitate the colouring matter: when this mixture has subsided, the clear part is poured off, the residue washed with alcohol, and these liquors filtered and distilled; they leave a brown alkaline residue, which is to be saturated by water slightly acidulated by sulphuric, hydrochloric, or acetic acid; the neutral liquor is then filtered off, concentrated by evaporation if necessary, and when cold precipitated by slight excess of ammonia; the precipitate is washed, and digested in warm dilute alcohol, to remove brucia; the remaining strychnia is then dissolved in boiling alcohol with a little animal charcoal, and filtered whilst hot; on cooling, the strychnia is deposited. (See DUMAS, v. 754, for an abstract of the other methods.)

When a solution of strychnia in common alcohol is left to slow evaporation, it yields the alkaloid in octoëdra, or four-sided prisms, terminated by pyramids; when rapidly crystallized it is granular. It is intensely bitter, and extremely poisonous, one-eighth of a grain being sufficient to kill a dog, and a quarter of a grain often producing a decided effect upon a healthy man. It produces, in larger doses, paroxysms of tetanus, and repeated convulsions, like those resulting from electric shocks. Injected in very small quantities into the veins, death very soon ensues, and in this way it is that the poisoned arrows of the Javanese produce their effect.

Strychnia is fusible, but not volatile, and easily decomposed by heat; subjected to destructive distillation it affords the usual products of these compounds. It is almost insoluble in cold water, and 1 part requires 2500 of boiling water for solution: the intensity of its bitterness is such, that its cold aqueous solution, which does not contain more than a six-thousandth of its weight of strychnia, may be diluted with 100 times its bulk of water, and yet remain sensibly bitter. It is soluble in common alcohol, but absolute alcohol, and ether, scarcely dissolve it when quite

free from acid. It is soluble in the acids, and forms soluble, colourless, and crystallizable salts*. When chlorine is passed through a mixture of strychnia and water, it is dissolved, and the solution yields colourless crystals of hydrochlorate of strychnia by evaporation: boiled with iodine and water it is also dissolved. Fused with sulphur it evolves sulphuretted hydrogen. Adopting Liebig's analyses, strychnia is an anhydrous compound of

Carbon	30	180	77.0	Liebig. 77.20
Hydrogen	16	16	6.8	6.72
Oxygen	3	24	10.2	10.13
Nitrogen	1	14	6.0	5.95
Strychnia	1	234	100.0	100.00

Hence we have 234 as the equivalent of strychnia, and its symbol ($^{50}car + 16h + 3o + n$).

SULPHATE OF STRYCHNIA. (STRY + S'.)—This salt, when crystallized from its neutral solution, is in small cubes; excess of acid renders it acicular. It becomes opaque by exposure to air, without losing weight; it may be fused without decomposition when carefully heated; it then loses about 3 per cent. This salt is excessively bitter; it dissolves in about 10 parts of water at 60°, and in less at 212°. According to Liebig it is anhydrous, and consists (dried at 212°) of

Strychnia	1	234	Liebig. 85.6
Sulphuric acid	1	40	14.4
Sulphate of strychnia	1	274	100.0

The other salts of strychnia are crystallizable, and mostly very soluble; even those with the oxalic and tartaric acids.

2. BRUCIA.—The presence of this alkaloid in the usual sources of strychnia, and the method of separating them, have already been described. It is most abundantly procured from the bark of the *Strychnos nux-vomica*, commonly called *false angustura*. This bark is coarsely powdered, and having been previously digested in sulphuric ether to free it from fatty matter, is treated by alcohol, the alcoholic solution evaporated, and the residue dissolved in water, saturated with oxalic acid, and evaporated to dryness. Alcohol, digested upon this residuum, dissolves colouring matter, and leaves pure oxalate of brucia, which may be decomposed by lime, and the brucia dissolved out by boiling alcohol, from which, by slow evaporation, it is obtained in crystals.

Brucia forms either prismatic or foliated crystals, according as it has been slowly or rapidly deposited: it is soluble in about 850 parts of cold,

* Nitric acid always reddens strychnia, but it is said that *pure strychnia*, (that from upas,) is not thus discoloured, and that the effect is due either to a yellow uncrystallizable compound, which generally accompanies strychnia, or to the presence of brucia. Be this as it

may, the effect of nitric acid upon all the samples of strychnia and its salts, which I have examined, has been to redden them: we are, however, as yet but imperfectly acquainted with this alkaloid and its combinations.

and in 500 of boiling water; its taste is strongly and permanently bitter; it is very soluble in alcohol, but insoluble in sulphuric ether: with the acids it forms soluble salts, mostly crystallizable; they are bitter, and are decomposed not only by the alkalis, but by morphia and strychnia, both of which precipitate the brucia. Brucia is reddened by nitric acid, and the colour changes to violet on the addition of protochloride of tin. A drop of bromine added to the alcoholic solution of brucia, renders it violet; by these characters it is distinguished from strychnia and from the other alkaloids. Anhydrous brucia consists of

Carbon	32	192	Liebig. 70·96
Hydrogen	18	18	6·50
Oxygen	6	48	17·40
Nitrogen	1	14	5·14
Anhydrous brucia	1	272	100·00

Hence we have 272 as the equivalent, and $(32\text{ car} + 18\text{ h} + 6\text{ o} + \text{n})$ as the formula of brucia.

Crystallized Brucia is a perfectly definite hydrate, including 6 atoms of water; its equivalent therefore is $272 + 54 = 336$.

SULPHATE OF BRUCIA ($\text{BRU} + \text{S}'$) is very soluble in water, and sparingly so in alcohol; it forms prismatic crystals, which are extremely bitter, and include 4 atoms of water, 2 of which they lose by efflorescence.

The general characters of the remaining salts of brucia have been above stated.

3. STRYCHNIC ACID.—This acid was obtained by Pelletier and Caventou as follows:—Powdered Ignatius' bean, or nux-vomica, was first digested in ether, and all soluble matters being removed, it was next treated by alcohol; the alcoholic solutions were evaporated, water added to the residue, and filtered; the filtered liquor was then digested with pure magnesia; an insoluble *strychnate of magnesia* was thus formed, which, washed with cold water and dried, was digested in alcohol to abstract free strychnia; the strychnate of magnesia was then dissolved in boiling water, rapidly filtered, and mixed, whilst hot, (for the salt is not soluble in cold water,) with acetate of lead: the resulting *strychnate of lead* was then decomposed by sulphuretted hydrogen, and the sulphuret of lead being filtered off, or allowed to settle, the solution was evaporated; it yielded a brown liquid, which deposited hard granular crystals of *strychnic acid*. Neither the equivalent nor the ultimate composition of this acid have been satisfactorily determined.

STRYCHNATES.—The *strychnates* of ammonia, potassa, and of soda, are very soluble both in water and in alcohol: when the aqueous solution of *strychnate of baryta* is evaporated, it yields spongy vegetations. The salts of iron, mercury, and silver, are not affected by neutral strychnate of ammonia, but it renders the solutions of copper green, and, after some time, a bright-green precipitate, scarcely soluble in water, falls: Pelletier and Caventou regard this character as distinctive of the strychnic acid.

IV. VERATRIA, AND OTHER ALKALOIDS.—In this subsection I include a long list of alkaloids, and of other substances apparently related to them, which have been more or less accurately examined, but the greater number of which require more minute investigation. They are extremely interesting to the chemist from the analogy which they bear to the well-defined alkaloids; and to the medical physiologist, as presenting, in an insulated state, the active principles of many important and energetic articles of the *Materia Medica*.

1. VERATRIA.—Veratria was discovered, in 1819, by Pelletier and Caventou (*Ann. de Ch. et Ph.*, xiv. 69), and, about the same time, by Meisner, in Germany. (*Schweigger's Jour.*, xxv. 377.) It is contained in the seeds of the *Veratrum sabadilla*, and the roots of the *Veratrum album*, or *white hellebore*, united with gallic acid*. It is most readily procured from the seeds of the *sabadilla*, which are first digested in ether, to remove oily matter, then boiled in alcohol, and the solution suffered to cool; it is then filtered, evaporated to dryness, and the residue digested in water: which, being partly evaporated, deposits a yellow matter, to be separated by filtration. The clear solution is now mixed with acetate of lead, which gives a precipitate, to be removed by filtering; and the filtered liquor (its lead having been separated by sulphuretted hydrogen, and heated) is now boiled with magnesia; the precipitate thus produced is digested in boiling alcohol, from which the veratria is deposited in a pulverulent form, on evaporation. If not at first white, it may be rendered so by a second solution, and by the aid of animal carbon. As thus procured, veratria is not crystallizable; it has a pungent, but not a bitter taste, and powerfully irritates the nostrils. A very small dose produces nausea and vomiting. It fuses at a temperature of 122°, and concretes, on cooling, into a translucent yellow mass. Boiling water does not take up more than a thousandth part of its weight, but it is readily soluble in alcohol, and less so in sulphuric ether. But in this state, veratria, according to Couerbe (*Ann. de Ch. et Ph.*, lii., 352), is still blended with other principles, two of which are abstracted by boiling water: of these, one is crystallizable, and termed *sabadilline*; the other is deposited on the evaporation of the mother liquor in the form of viscid drops of a reddish colour and acrid taste: he has termed it *resinigomme de sabadillinet*. The alkaline residue of the veratria remaining after this treatment, is digested in successive portions of ether, and when these ethereal solutions are spontaneously evaporated, they deposit a white viscid matter, which is now *pure veratria*: the matter which resists the action of ether is called by Couerbe, *veratrin*. Pure veratria consists, according to Couerbe, of

* Veratria has also been discovered in the bulb of the *Colchicum autumnale* or *meadow saffron*, and is probably the principle to which the curative powers of that drug, in cases of gout, are referable. It is curious that, many years ago, Mr. Moore suspected the active ingredient in the celebrated French gout-specific, called *Eau Médicinale d'Husson*,

and which is a vinous infusion of colchicum, to be derived from hellebore, which we now know to contain the same alkaline base as colchicum.

† From the oil of the seeds of *sabadilla*, Pelletier and Caventou obtained, by the process of saponification, a peculiar fat acid, which they termed *cevadie acid*.

Carbon	34	204	Couerbe.
Hydrogen	22	22	71.24
Oxygen	6	48	7.52
Nitrogen	1	14	16.39
			4.85
Veratria	1	288	100.00

The equivalent, therefore, of veratria, is 288, and its formula ($^{34}car + ^{22}h + ^{60}o + n$).

SALTS OF VERATRIA.—Veratria forms compounds with the acids, which are very difficult of crystallization. Couerbe succeeded in obtaining a crystallizable *sulphate of veratria* ($VER + S'$), from the analyses of which he established the equivalent of veratria as above. The *hydrochlorate of veratria* is also a crystallizable salt.

2. ATROPIA.—The existence of an alkaloid in the *Atropa belladonna*, or *deadly nightshade*, was first shown by Brandes, in 1819, (*Schweigger, Jour.*, xxviii.,) and the process for obtaining it was afterwards improved by Mein (*Jour. de Phar.*, xx. 87), in consequence of Runge's discovery of the destructibility of some of these bases by the fixed alkalis.

The following is the process:—80 parts of the powdered root of belladonna, from plants two or three years old, are digested in 60 parts of alcohol (0.830) for several days; the alcohol is then pressed out, and the residue treated by fresh alcohol. The tinctures are mixed, filtered, and 1 part of slaked lime is added, the whole being left for 24 hours and then filtered. Sulphuric acid is then dropped in in slight excess, and the resulting sulphate of lime separated by filtration. Distil off half the filtered liquor, add 6 parts of water to the residue, and drive off the remaining alcohol by heat: concentrate carefully to one-third its bulk, and when cold, drop into the liquor a strong solution of carbonate of potassa as long as it precipitates the atropia, which falls in a gelatinous form; it may be freed from mother-water by pressure in bibulous paper, dried and dissolved in 5 parts of alcohol; filter, and dilute with 6 of water; evaporate the alcohol and set the remaining solution aside, when the atropia forms yellowish crystals: 1000 parts of the root yield about 3 of the alkaloid.

Atropia crystallizes in silky prisms: it is soluble in anhydrous alcohol and in ether, and in about 500 parts of cold water; this solution is bitter, and when dropped into the eye, dilates the pupil.

Atropia forms definite compounds with the acids; the sulphate and acetate are more crystallizable than the hydrochlorate or nitrate: the salts are decomposed, and the atropia thrown down by potassa and ammonia, by infusion of galls, and by chlorides of gold and platinum, with which it forms compounds gradually crystallizing, and probably composed of hydrochlorate of atropia combined with the metallic chloride.

When atropia is heated with potassa it is easily decomposed, and abundance of ammonia is evolved. The facility with which this alkaloid is thus destroyed, renders the use of caustic alkalis in its preparation inadmissible. According to Liebig, the ultimate composition of atropia is ($^{68}car + ^{23}h + ^{12}o + n$), but the nature and properties of this body require further examination.

3. **HYOSCYAMIA.**—This alkaloid was obtained by Brandes from the seeds of the *Hyoscyamus niger*; an alcoholic solution or tincture of which is mixed with a small quantity of lime, and the precipitate digested in dilute sulphuric acid; the solution, containing sulphate of hyoscyamia, is then decomposed by the addition of powdered carbonate of soda; the hyoscyamia is thus precipitated, and it is quickly removed from the solution and dried by pressure in blotting-paper; it is then dissolved in absolute alcohol, filtered through animal charcoal, and the solution evaporated, a little water being added towards the end of the process.

Hyoscyamia is described as forming silky crystals, difficultly soluble in water, of an acrid and nauseous taste, highly poisonous, and, when applied to the eye, producing a dilated pupil. It is easily decomposed, with the evolution of ammonia, by the fixed alkalis. It is very soluble in alcohol and ether: its salts are said to be neutral and crystallizable. (GEIGER and HESSE, *Jour. de Pharm.*, xx. 92.)

4. **SOLANIA.**—This alkaloid was discovered by Desfosses of Besançon, in the berries of the *Solanum nigrum*, and in the leaves of the *Solanum dulcamara*. (*Jour. de Pharm.*, vi. and vii.) The filtered juice of the ripe berries was saturated by solution of ammonia, which threw down a gray powder: this was dissolved in boiling alcohol, filtered through animal charcoal, and evaporated, when the solania was deposited. Solania is white and pulverulent, and though, like several of these substances, it has no direct alkaline action upon turmeric, it restores the blue of reddened litmus. Acted on by caustic potassa it evolves ammonia. It is precipitated from its acid solutions by the alkalis, and does not form crystallizable salts. It has been analyzed by Blanchet, who states its components to be per cent. 62 carbon, 8·9 hydrogen, 1·6 nitrogen, and 27·5 oxygen. Upon the whole, our information upon the subject of solania is very incomplete.

5. **DATURIA.**—Daturia was discovered by Brandes in the seeds of the *Datura stramonium*. Geiger and Hesse obtained it by the same process as that for procuring hyoscyamia. (*Jour. de Pharm.*, vi. and xx.) The following process is given by Simes, for its extraction. A pound of stramony seeds, in fine powder, was boiled for an hour in 3 quarts of weak alcohol; to the liquor, filtered whilst hot, half an ounce of magnesia was added, and the mixture shaken from time to time for 24 hours; the precipitate was then collected, boiled for some minutes with 12 ounces of alcohol, and filtered through animal charcoal; this alcoholic solution was then evaporated to half its bulk, and set aside for 24 hours, when it was found to have deposited globules of oil and crystals of colourless daturia; this deposition continued during the spontaneous evaporation of the liquor, when the daturia was collected, dissolved in acidulated water, filtered through charcoal, precipitated by magnesia, again dissolved by alcohol, and obtained in a pure form. Daturia crystallizes in colourless quadrangular prisms, of a bitter and acrid taste, and is very poisonous; applied to the eye, the pupil is durably dilated. Its aqueous solution is decidedly alkaline. It is soluble in about 280 parts of cold, and 72 of boiling water, and readily soluble in alcohol.

The Salts of Daturia are generally soluble, crystallizable, and perma-

nent in the air; they are decomposed by the alkalis, and daturia falls in white flocculi. Dumas, adverting to the analogy that subsists between daturia, atropia, and hyoscyamia, suggests the possibility of their identity: their ready decomposition by the fixed alkalis approximates them to the ammides; and it seems probable that a more accurate knowledge of their ultimate composition may throw light upon the subject of the alkaloids in general.

6. **PICROTOXIA.**—This name has been given to a poisonous bitter substance, discovered by Boullay, 1819, in the berries of the *Menispermum cocculus*, or *Cocculus indicus*. It may be obtained by the following process: Add acetate of lead to a decoction of the berries, as long as any precipitate falls; filter, evaporate, and digest the extract in highly-rectified alcohol; evaporate to dryness, and agitate the remaining matter with a little water; the picrotoxia remains in the form of a white residue of a bitter taste.

Picrotoxia is difficultly soluble in water. Alcohol, of the specific gravity of $\cdot 810$, dissolves one-third its weight. It is soluble in weak solutions of the pure alkalis. Picrotoxia was originally described by Boullay as a salifiable base, and as united in the seeds to a peculiar acid, which was termed *menispermic acid*. Casaseca has shown that this acid is a mixture of malic and sulphuric acids, and that picrotoxia has no alkaline reaction, and does not neutralize the acids; but it certainly appears to form definite compounds with the acids, some of which are crystallizable. Its ultimate composition has not been accurately ascertained; but, according to Opperman, it does not contain nitrogen, but consists of 61.5 carbon, 6.1 hydrogen, and 32.4 oxygen per cent.

7. **NICOTINA.**—This principle was obtained by Vauquelin, by the following process (*Ann. de Ch.*, lxxi.): Evaporate the expressed juice of fresh tobacco leaves to one-fourth its bulk; and, when cold, strain it through fine linen; evaporate nearly to dryness; digest the residue in alcohol; filter and evaporate to dryness; dissolve this again in alcohol, and again reduce it to a dry state. Dissolve the residue in water, and saturate the acid which it contains with weak solution of potassa, introduce the whole into a retort, and distil to dryness; redissolve, and again distil three or four times successively. The nicotina will thus pass into the receiver, dissolved in water, from which solution it may be obtained by very gradual evaporation; or it may be saturated by sulphuric acid, and the sulphate of nicotina, so formed, decomposed by the addition of lime and distillation; a mixture of nicotina, ammonia and water, passes over, from which the nicotina may be abstracted by agitation with ether, and this ethereal solution, when distilled, leaves the nicotina.

Nicotina, in its purest state, is a transparent colourless liquid, of a pungent and disagreeable odour, and acrid taste; it is alkaline; volatile at 212° ; soluble in all proportions in water, alcohol, and ether, and, when its aqueous solution is agitated with ether, the greater part of it leaves the water, and is retained by the ether. It is very poisonous, and forms distinct salts with the alkalis. It has been but imperfectly examined,

and, from the method of obtaining it, it appears doubtful whether it is an original proximate principle of tobacco.

8. CONIA.—It appears from the experiments which have been made upon hemlock, that its active principle resides in a volatile and uncrySTALLIZABLE alkaloid; its properties have been investigated by Geiger (*Journal für Pharmacie*, xxv.), by Boutron-Charlard and O. Henry (*Ann. de Ch. et Ph.*, Lxi. 337), and by Dr. Christison (*Edin. Phil. Trans.*, 1836, p. 383), whose paper upon the subject includes some valuable physiological experiments. When the seeds or leaves of hemlock are distilled with water, the fluid which passes over has the odour of the plant, but is not poisonous; on the contrary, when caustic lime or potassa are previously added to the green seeds or leaves and distilled with water at as low a temperature as possible, the liquid which passes over is strongly alkaline and poisonous: when 10 or 12 lbs. of the seeds are worked at once, an oily matter comes over at first which is nearly pure conia, but the greater part of the alkaloid is dissolved in the distilled water; if this be redistilled, it loses a little of its strength; but if previously neutralized by an acid, such as the sulphuric, the poisonous principle becomes fixed, and water alone distils over. The residue consists of sulphate of conia, sulphate of ammonia, and resin, the latter being produced by the decomposition of part of the conia. To obtain the conia, the above residue is digested in a mixture of 2 parts of alcohol and 1 of ether, which leaves the sulphate of ammonia; and then, the alcohol and ether being carefully distilled off, the remaining sulphate of conia is heated gently with a little water and caustic potassa, when there is obtained in the receiver a watery solution of conia in the lower part, and floating on this, a layer of nearly pure hydrate of conia, containing a trace of ammonia; the water may be abstracted by chloride of calcium, and the ammonia by exposure in vacuo.

Conia, thus obtained, has the appearance of a colourless volatile oil, lighter than water, of a powerful diffusible odour, somewhat like that of hemlock, and intensely acrid to the taste. It has a strong alkaline action on reddened litmus and turmeric. It is readily soluble in diluted acids, which it neutralizes, but its salts have not been crystallized. It is sparingly soluble in water, and combines with about a fourth of its weight of water to form a *hydrate*. This hydrate, and its aqueous solution, become opaque when slightly heated, and again transparent on cooling. Exposed to air, conia soon becomes brown, and is slowly resolved into a resinous matter, with the disengagement of ammonia; heat accelerates this change, so that it requires to be carefully excluded from air. It readily distils over with water at 212° , but its boiling point is 370° , and it cannot be distilled, either alone or with water, without a considerable part being decomposed. It contains, according to Liebig, 66.91 carbon, 12.0 hydrogen, 8.28 oxygen, and 12.8 nitrogen.

Dr. Christison observes that conia is most abundantly obtained from the seeds, fully developed, but still green; even from these, however, the quantity is small; from 40 pounds he obtained two ounces and a half of hydrated conia; but it probably exists in the plant in larger proportion,

for much of it is always decomposed in the processes of separation, as is indicated by the evolution of ammonia.

Geiger observed that the *dried* leaves of hemlock contain no conia, and that it is not to be found in many specimens of the extract, hence the discrepancies respecting its efficacy. According to Dr. Christison the extract becomes feeble or inert in two ways; either by having been over heated towards the end of the process, or by long keeping, exposed to air; in both cases ammonia is formed, and extracts well prepared at first, become inert in a few years. To ascertain if conia be present, the extract, or other preparation, may be triturated with solution of potassa, upon which the odour of conia, if present, is strikingly perceptible. The alcoholic extract of the ripe seeds appears to be most efficacious. Probably some salt of conia will prove to be the most effective and convenient form for its medical use.

Conia is a deadly poison to every order of animals; it first palsies the voluntary muscles, then the respiratory muscles and the diaphragm, thus ending in death by asphyxia. The heart continues to act after other signs of life are extinct. Few poisons equal it in subtilty or swiftness; a drop put into the eye of a rabbit, killed it in nine minutes. 3 drops, in the same way, killed a strong cat in a minute and a half. 2 grains of conia, neutralized with hydrochloric acid, and injected into the femoral vein of a young dog, produced almost instant death: "in two seconds, or three at furthest, and without the slightest warning struggle, respiration had ceased, and with it all external signs of life."

Conia is probably combined in the recent plant with some vegetable acid, the nature of which has not, however, been ascertained.

9. ACONITA.—This is an extremely poisonous and active alkaloid, extracted from the aconite; it is probably contained in several species of that plant. The following directions for its preparation are given in the *London Pharmacopœia*: "Take of the root of aconite, dried and bruised, 2 pounds; rectified spirit, 3 gallons; diluted sulphuric acid, solution of ammonia, purified animal charcoal, of each as much as may be sufficient. Boil the aconite for one hour with a gallon of the spirit, in a retort to which a receiver is adapted; pour off the liquor, and again boil the residue with another gallon of the spirit, and with that which had distilled over, and also pour off the liquor. Let the same be done for a third time. Then press out the aconite, and having mixed all the liquors, strain them, and distill off the spirit. Evaporate what remains to the proper consistency of an extract. Dissolve this in water, and strain. Evaporate the liquor by a gentle heat, till it acquires the consistency of syrup. To this, add a sufficient quantity of dilute sulphuric acid, mixed with water, to dissolve the aconitina. Then drop in the solution of ammonia, and dissolve the precipitated aconitina in dilute sulphuric acid and water, mixed as before. Afterwards mix the animal charcoal, occasionally shaking the mixture during a quarter of an hour. Lastly, strain, and again drop in solution of ammonia to precipitate the aconitina, which is to be washed and dried."

Mr. Pereira states that this substance, as prepared by Mr. Morson, presents the following properties. "It is a white, odourless solid, either

dull and amorphous, or somewhat sparkling, and apparently crystalline. As it is usually described as being uncrystallizable, I have carefully examined a supposed crystalline mass with the microscope, but I could not detect distinct crystals. The fragments appeared like thin plates of chlorate of potash, and though they varied greatly in shape, the triangular form seemed predominant. Heated in a tube, aconita readily fuses, and forms a pale amber-coloured liquid; and at a higher temperature decomposes. It is not volatile. Heated on platinum, or over a spirit-lamp, it is speedily and entirely dissipated. It is soluble in alcohol, ether, and the acids. From its acid solution it is precipitated by ammonia. A minute portion of it mixed with lard, and applied to the eye, causes contraction of the pupil, as I have repeatedly seen. Geiger and Hesse state that the aconitina which they obtained produces dilatation of the pupil. Mr. Morson's aconitina is so powerful that one-fiftieth of a grain has endangered the life of an individual. It is the most virulent poison known, not excepting hydrocyanic acid."

[10. DIGITALIA.—Leroyer gives the following directions for the extraction of digitalia: He takes "one livre of digitalis purpurea, and first treats it with cold ether, and then with the same agent heated in a close stove, in order that the temperature may be more easily raised. The tinctures obtained in this manner, were, after filtration, of a greenish-yellow colour and a bitter taste; the residue from their evaporation has a resinous appearance, and is insupportably bitter, producing upon the tongue a sensation of numbness like that which is experienced from chewing aconite. Exposed to the air, this residuum powerfully absorbs moisture. When taken up by distilled water, it divides into two parts; the vehicle holds one of them in solution, the other is precipitated, and presents all the characters of chlorophylle; the aqueous solution of the ethereal residue reddens turnsol paper. Hydrate of protoxide of lead was then added to neutralize the free acid thus indicated, and to separate from the bitter principle that which is apparently combined with it. The salt of lead thus formed was soluble, and consequently could not be separated from the bitter principle; several earths were tried for the same purpose, but with no better success; it was therefore necessary to resort to another method. After evaporating to dryness the portion treated by the lead, it was again dissolved in highly-rectified ether; by this operation he obtained the bitter principle of digitalis disengaged from those substances with which it was united. By evaporating this solution a brown heavy substance is obtained, that restores, though slowly, the blue of turnsol-paper reddened by an acid. If in this last-mentioned character, as well as in its bitterness, it approaches the alkaloids, its extreme deliquescence separates it from them." This deliquescence prevents it from crystallizing in a distinct and permanent manner; but Leroyer thinks that it does crystallize regularly under favourable circumstances. Prevost having placed a drop of the solution of digitalia in alcohol on a piece of glass, and cautiously evaporated it by means of a spirit-of-wine lamp, detected with a microscope numerous and well-defined crystals of various forms. The same observer states, that the basic form of them all appeared to be a straight prism with rhomboidal base.

11. DELPHIA.—This alkaloid was discovered, in 1819, by Lassaigne and Feneulle, in the seeds of the *Delphinium staphysagria*, or *Stavesacre*. (*Ann. de Ch. et Ph.*, xii. 358.) The simplest mode of obtaining it is that suggested by Berzelius: digest the bruised seeds in water acidulated by sulphuric acid, then add magnesia, collect and dry the precipitate, and digest it in alcohol, by which the delphia is taken up: it may be purified by boiling it in the state of sulphate, with animal charcoal, and precipitating by ammonia, which throws it down in a gelatinous form: obtained by evaporating its alcoholic solution, it is a crystalline powder, which becomes opaque when dried.

Delphia, when pure, is very difficultly soluble in water at any temperature: it is soluble in alcohol, and somewhat less so in ether. It has a peculiarly acrid taste, and excites a burning sensation in the throat. Its salts are very pungent and bitter, and most of them very soluble. Delphia has been analyzed by Couerbe (*Ann. de Ch. et Ph.*, lii. 359), with the following results:—

				Couerbe.
Carbon	27	162	77.00	
Hydrogen	19	19	8.89	
Oxygen	2	16	7.50	
Nitrogen	1	14	6.61	
Delphia	1	211	100.00	

Couerbe discovered another principle in the stavesacre seed, which he has termed *Staphisain*: in ultimate composition it appears to resemble the alkaloids, but it is not salifiable. It is separable from delphia by the action of ether, in which it is insoluble.

12. CORYDALIA.—This alkaloid was discovered by Wackenroder in the *Corydalis tuberosa*. (*Phil. Mag. and Ann.*, iv. 153.) It is contained in the plant, in combination with malic acid, from which it may be separated by magnesia, and purified by solution in alcohol. It forms prismatic crystals, soluble in alcohol and ether, but very sparingly so in water; it is tasteless, but its salts are bitter; they are decomposed by the alkalis, and by infusion of galls.

13. SANGUINARIA.—The root of the *Sanguinaria canadensis*, or *Blood root*, contains, according to Dana (*Phil. Mag. and Ann.*, v. 151), an alkaloid, which may be separated as follows: the red alcoholic tincture of the powdered root is mixed with a little ammonia, and poured into water; the matter which subsides yields the alkali to hot alcohol; it must be purified by animal charcoal. It is white, acrid, insoluble in water, but soluble in alcohol and ether, and alkaline to tests. Its salts have a red colour.

14. CYNAPIA.—Under this name an alkaloid, obtained from the *Aethusa cynapium*, has been described by Professor Ficinus, of Dresden. It forms prismatic crystals soluble in water and alcohol, but insoluble in ether: it is salifiable.

15. EMETINA.—This term implies the active or emetic principle of *Ipecacuanha*, from which it was procured by Pelletier and Majendie, in

1817. Boullay has since detected it in the root of the *Violet* (*Viola odorata*), and Torreri in the root of the *Iris florentina*.

Emetina is obtained by digesting powdered ipecacuanha root, first in ether, by which a fatty matter is abstracted (which gives ipecacuanha its nauseous odour, but which is not emetic), and then in alcohol; this tincture is mixed with magnesia, which throws down impure emetina: the deposit is washed with cold water, and redissolved in boiling alcohol, from which solution the emetina is obtained by evaporation or distillation. Berzelius proposes to digest the powdered root in dilute sulphuric acid, precipitate by magnesia, and separate the emetina by alcohol as before; but this process has not, I believe, been adopted. Emetine is a yellow uncrystallizable substance, of a bitter taste, fusible at about 125° , almost insoluble in cold water and in ether, but soluble in alcohol; it has an alkaline reaction, but its salts have not been satisfactorily crystallized. It is powerfully emetic. The French chemists have given the name *Violine* to the emetine of the violet root. According to Caventou, the emetic action of emetine is prevented by infusion of galls, and the *gallate of emetina* is insoluble*.

§ XIX. CRYSTALLIZABLE AND OTHER PRINCIPLES NOT SALIFIABLE, BUT IN SOME RESPECTS ANALOGOUS TO THE ALKALOIDS.

1. SALICIN. ($42\text{ car} + 29\text{ h} + 22\text{ o}$).—This substance was extracted, in 1830, from the bark of the willow (*Salix helix*), by M. Leroux. It exists in several species of willow; and, according to Braconnot, in the bark of the poplar, especially the *Populus tremula* (Populin?)

It is obtained by adding subacetate of lead to a decoction of willow-bark, as long as a precipitate falls, filtering, boiling with chalk, filtering a second time, and evaporating the solution, when the salicin crystallizes.

Salicin forms white prismatic crystals, fusible below 212° , and not losing weight at 300° , of a bitter taste, insoluble in ether, sparingly soluble in cold, but readily so in hot water and alcohol; it is neither acid nor alkaline; with sulphuric acid, it acquires a deep red colour.

When salicin is boiled in dilute hydrochloric or sulphuric acid, a white powder is formed, termed by Piria *Saliretine*, and at the same time grape sugar is produced, the decomposition being such that 1 atom of salicin ($42\text{ car} + 29\text{ h} + 22\text{ o}$) is converted into 1 atom of saliretine = ($30\text{ car} + 15\text{ h} + 8\text{ o}$), and 1 atom of grape sugar = ($12\text{ car} + 14\text{ h} + 14\text{ o}$).

When chlorine is passed through a cold aqueous solution of salicin, a crystalline yellow powder is deposited, readily soluble in hot alcohol, but

* Several analyses have been made of different species of ipecacuanha (and there are several known in the drug-trade), by MM. Pelletier and Majendie, and an account of their researches is published by M. Robiquet (*Ann. de Ch. et Ph.*, iv. 172); 100 parts of the brown wrinkled variety of this root, deprived of the comparatively inert

woody fibre which traverses its centre, afforded

Fatty matter	2
Emetine	14
Gum	16
Starch	18
Woody fibre	48
A trace of wax	
Loss	2

difficultly in water; it has been called *Chlorosalicine*; its ultimate constitution is such, that it may be represented as salicin, in which 4 equivalents of hydrogen are replaced by 4 of chlorine, its formula being ($42\text{ car} + 25\text{ h} + 4\text{ c} + 22\text{ o}$). When chlorine is passed into a solution of salicin heated to 140° , a heavy oily compound is formed, which contains more chlorine and less oxygen than the preceding, its formula being ($42\text{ car} + 18\text{ h} + 7\text{ c} + 19\text{ o}$).

SALICULE.—Piria (*Ann. de Ch. et Ph.*, LXIX. 281) found a peculiar acid amongst the products of the decomposition of salicin, which he regarded as a *hydruret of salicule*, and Ettling afterwards showed that this product is identical with the essential oil of the flowers of the common meadow-sweet (*Spiræa ulmaria*) which had been called *hydruret of spiroyle*, and that in ultimate composition both *salicule* and *spiroyle* (the bases of these hydrurets) may be regarded as oxide of benzule, containing 1 atom more of oxygen than the anhydrous benzoic acid.

These analogies will be evident from the following formulæ:—

Benzule	($14\text{ car} + 5\text{ h} + 2\text{ o}$)
Benzoic acid	($14\text{ car} + 5\text{ h} + 3\text{ o}$)
Salicule (and spiroyle)	($14\text{ car} + 5\text{ h} + 4\text{ o}$)
Hydruret of salicule (and oil of spiræa)	($14\text{ car} + 5\text{ h} + 4\text{ o}$) + h .

Whence it appears that the hydruret of salicule and the volatile oil of spiræa (which are acids, and combine with bases) are isomeric with the hydrated or crystallized benzoic acid, the formula of which is ($14\text{ car} + 5\text{ h} + 3\text{ o}$) + ($\text{h} + \text{o}$). The term *saliculous acid* has been applied to the above hydrurets, and the *saliculites* are obviously isomeric with the benzoates, but differ from them in their properties.

SALICULOUS ACID. HYDRURET OF SALICULE. HYDRURET OF SPIROYLE. More properly *hydrosaliculic acid*, represented by the formula ($14\text{ car} + 5\text{ h} + 4\text{ o}$) + h .—Obtained, 1. By distilling a mixture of 2 parts of bichromate of potassa, 2 of salicin, 5 of sulphuric acid, and 40 of water. The salicin is dissolved in the diluted acid, and the whole mixed in a retort, when slight effervescence ensues, from the formation of carbonic acid and of formic acid; distillation is then commenced, and the saliculous acid passes over with the water; it is purified by washing and distillation off chloride of calcium; (8 ounces of salicin give 2 of the acid.) (PIRIA.) 2. Distil the volatile oil of the *Spiræa ulmaria* with excess of solution of potassa, as long as oil passes over; supersaturate the residue (which is solution of saliculite of potassa) with dilute sulphuric acid, and redistill, when the saliculous acid passes over with the water. (PAGENSTECHE.)

Saliculous acid thus obtained is a pale yellow, oily, inflammable liquid; sp. gr. 1.173, boiling at 370° , and freezing at -4° . It has an acid taste, an agreeable odour, is somewhat soluble in water, and in all proportions in alcohol and ether; it first reddens and then bleaches litmus; sulphuric acid decomposes it; in contact with chlorine and bromine, it loses 1 equivalent of hydrogen, forming hydrochloric and hydrobromic acids, and acquires 1 of chlorine or bromine, producing

chlorosaliculic and bromosaliculic acids. Treated with excess of hydrate of potassa it gives off hydrogen, and saliculic acid is formed.

Saliculous acid combines with metallic oxides, in which case its hydrogen is replaced by the metal, or it loses an atom of water, which is replaced by the metallic oxide. Its salts, with the fixed alkalis, are soluble and alkaline, the other salts are insoluble; it transiently colours the persalts of iron purple, and gives a green precipitate with acetate of copper. All the saliculites are decomposed, and saliculous acid evolved by the stronger acids. (See LIEBIG, and the authorities quoted, for an account of the saliculites.)

SALICULIC ACID is the result of the action of potassa on saliculous acid; the mixture is at first brown, but when heated evolves hydrogen and becomes white; it is then dissolved in water, and treated by a mineral acid, which separates the saliculic acid, and which must be purified by repeated crystallization. It sublimes without decomposition, forming acicular crystals like those of benzoic acid, difficultly soluble in cold water, but easily in hot water and in alcohol. Its formula, when anhydrous, is $(14\text{ car} + 5\text{ h} + 5\text{ o})$. With nitrate of silver it yields an insoluble *saliculate of silver*, the formula of which is $(14\text{ car} + 5\text{ h} + 5\text{ o}) + (\text{ag} + \text{o})$.

2. PHLORIZIN.—This term (derived from *φλοιος*, *bark*, and *ρίζα*, *root*,) has been applied to a crystallizable substance extracted from the bark of the roots of the pear, plum, cherry, and apple trees; it gives them their bitter astringency, and is associated, especially in the cherry-root bark, with a peculiar red colouring matter; it is also found, but in very small quantity, in the bark of the trunk and branches, and even in the leaves. It is obtained by boiling the bark recently stripped from the roots of the apple tree for four or five hours in water sufficient to cover it, then pouring off the decoction, and suffering it to stand at rest for twenty-four or thirty-six hours, when a large quantity of coloured phlorizin is deposited in the form of granular crystals, which may be discoloured by treatment with animal charcoal. Or the bark may be digested for seven or eight hours in proof spirit, at a temperature between 120° and 140° , which, on cooling, yields whiter crystals, and a second crop may be obtained from the mother liquor. Care must be taken to avoid acid and alkaline liquors, and vessels of lead or iron.

Phlorizin forms groups of colourless or yellowish crystals, of a sweetish bitter astringent taste; its sp. gr. is 1.4293. It is difficultly soluble in cold water, requiring about 1000 parts at 32° , but boiling water dissolves it in all proportions, so that it is easily obtained in a crystalline mass by cooling a saturated solution; it is more soluble in cold alcohol, and water throws it down in crystals from its alcoholic solution. It is sparingly soluble in ether at all temperatures. These solutions have no alkaline reaction. In its ordinary state it contains about 7 per cent. of water, which it loses when dried at 212° . At 342° it enters into perfect fusion, and at 388° it begins to be decomposed, producing a little benzoic acid, which sublimes, together with pyroacetic spirit, carbonic acid, and a brown oil; the residue is charcoal. If suddenly heated to between 400° and 500° , it fuses into a yellow transparent

substance, and loses its property of crystallizing, and if the heat be continued, its physical and chemical properties are further changed. When dry, it is immediately decomposed and charred by sulphuric acid; nitric acid converts it into oxalic acid, and dilute nitric acid gradually changes it into a yellow matter resembling the colouring matter with which it is originally associated in the bark. Hydrochloric acid converts it into a red insoluble matter. Acetic acid dissolves it, and the alkalis throw it down unaltered. Chlorine yields a white precipitate in its aqueous solution.

Phlorizin is soluble in the caustic alkaline solutions, and the acids precipitate it. Persulphate of iron renders the solution of phlorizin dark brown; subacetate of lead occasions an abundant precipitate, which, when dry, is pale yellow; the compound may be called *phlorizate of lead*. It is not precipitated by neutral acetate of lead, chloride of mercury, or nitrate of silver, nor by gelatin or albumen. Its ultimate components are, according to Koninck ($14\text{ car} + 9\text{ h} + 9\text{ o}$). (*Ann. de Ch. et Ph.*, lxi. 151.) The phlorizate of lead consisted of 57.26 oxide of lead, 42.74 phlorizin; numbers which are equivalent to 2 atoms of oxide of lead + 1 phlorizin. But Stass (*Ann. de Ch. et Ph.*, lxix. 367) has added some important information to the history of this substance, and his ultimate analysis is very different from that of Koninck. According to Liebig, in composition, as well as properties, it is closely connected with salicin; he represents it as crystallized salicin + 2 atoms of oxygen, by the formula ($42\text{ car} + 29\text{ h} + 24\text{ o}$). Boiled with dilute sulphuric or hydrochloric acid, it yields grape sugar and *phloretine*: moistened with ammonia and exposed to air, it absorbs oxygen and becomes blue, and if then dissolved in ammonia, the solution yields a red powder on addition of acids, which is the substance called by Stass *phlorizeine*, the formula of which is ($42\text{ car} + 29\text{ h} + 26\text{ o} + 2\text{ n}$).

3. PIPERIN.—This substance was discovered by Oersted, in 1819 (*Journ. de Phys.*, xc.), and afterwards examined by Pelletier; it is obtained from *black pepper*. (*Ann. de Ch. et Ph.*, xvi.) Vogel gives the following process for its extraction: Digest 16 ounces of coarsely-powdered pepper for forty-eight hours in twice its weight of water, five times in succession; press out and dry the insoluble portion, and digest it for three days in 24 ounces of alcohol; press out this solution, filter, and evaporate it to the consistence of syrup: crystals are deposited, which are to be freed from adhering resin by ether, redissolved in alcohol, purified by animal charcoal, and recrystallized.

Piperin is a crystallizable substance, generally of a pale straw colour, and in the form of four-sided prisms, insoluble in cold, and slightly soluble in hot water; readily soluble in alcohol, and less so in ether. It fuses at a little above 212° . It dissolves in, but does not combine with, the acids: dissolved in acetic acid, it is left, on evaporation, in plumose crystals. It consists, according to Göbel, of 80.95 carbon, 8.13 hydrogen, and 10.92 oxygen.

4. ASPARAGIN.—This principle was discovered in asparagus, by Vauquelin and Robiquet (*Ann. de Ch.*, lvii.); and was shown by Plisson to be identical with a substance found by Robiquet in liquorice root,

which he named *Agedoite* (*Ann. de Ch.*, LXXII.), and also with the *Althein*, discovered by Bacon. (*Ann. de Ch. et Ph.*, XXXIV.) It has been found by Link in the *Ornithogalum*, and by Blondeau in the *Symphytum officinale*.

It is best obtained from asparagus, the juice of which is expressed, evaporated to the consistency of syrup, and set aside; it deposits crystals, which are purified by solution in water and recrystallization.

Asparagin forms transparent prismatic crystals, which are hard, brittle, of a cooling and somewhat nauseous taste, neither alkaline nor acid; soluble in 58 parts of cold water, and more soluble in hot; insoluble in anhydrous alcohol, and in ether. The crystals lose about 12 per cent. of water when heated: they evolve ammonia when triturated with caustic potassa, and nitric acid converts them into a bitter matter. According to Liebig, *anhydrous* asparagin consists of

					Liebig.
Carbon	8	. . .	48	. . .	36·4
Hydrogen	8	. . .	8	. . .	6·0
Oxygen	6	. . .	48	. . .	36·4
Nitrogen	2	. . .	28	. . .	21·2
<i>Anhydrous asparagin</i>	1		132		100·0
					100·00

The crystals include 2 atoms of water.

ASPARTIC ACID.—When asparagin is long boiled with hydrated oxide of lead, magnesia, or other bases, it is resolved into ammonia, and into a new acid, called the *aspartic acid*; and yet asparagin is not, as might be supposed, an *aspartate of ammonia*, because the alkalis do not immediately separate ammonia from it, nor do acids throw down aspartic acid when added to its aqueous solution.

When the *aspartate of lead* is decomposed by sulphuretted hydrogen, the *aspartic acid* is separated in the form of a white crystalline powder, consisting of 1 atom of anhydrous acid and 2 of water. The *anhydrous* aspartic acid consists of

					Liebig.
Carbon	8	. . .	48	. . .	41·7
Hydrogen	5	. . .	5	. . .	4·4
Oxygen	6	. . .	48	. . .	41·7
Nitrogen	1	. . .	14	. . .	12·2
<i>Anhydrous aspartic acid</i>	1		115		100·0
					100·00

Hence we see that 1 atom of anhydrous asparagin = 132, contains the elements of 1 atom of aspartic acid = 115, and 1 of ammonia = 17: or

$$(8 \text{ car} + 8 \text{ h} + 6 \text{ o} + 2 \text{ n}) = (8 \text{ car} + 5 \text{ h} + 6 \text{ o} + \text{n}) + (3 \text{ h} + \text{n}).$$

5. DAPHNIN.—The existence of an acid crystallizable principle in mezereon (*Daphne mezereon*), was first shown by Vauquelin (*Ann. de Ch.*, LXXIV.), and afterwards its properties were further examined by C. G. Gmelin and Bär, in 1822. A decoction of mezereon bark is precipitated by subacetate of lead, and the washed precipitate decomposed by sulphuretted hydrogen: the solution is then filtered, evaporated, and the residue digested in cold anhydrous alcohol, from which daphnin crystallizes, leaving malic acid and colouring matter.

Daphnin, purified by washing with cold alcohol, solution in water, and recrystallization, forms colourless crystals, bitter, but neither alkaline nor acid; soluble in hot, and sparingly in cold water, soluble in alcohol and ether, converted into oxalic acid by nitric acid, and fusible before it decomposes by heat.

6. CAFFEIN.—*Coffee* has been the subject of many chemical researches, and in 1821 a peculiar crystallizable principle was extracted from it by Pelletier and Caventou, and by Robiquet and Runge, previous to which, Schrader had published an analysis of *coffee beans*, of which the following is an abstract. (BERZELIUS, *Lehrbuch*, iv.) He found that 8 ounces of *raw coffee* distilled with water, gave a turbid and odorous distilled water, but the quantity of oil which probably produced these effects was too small to collect. The decoction in the retort was filtered, and was then of a yellow green colour: it was evaporated to syrup consistence, and mixed with alcohol, sp. gr. 0·85, as long as this occasioned a precipitate. The filtered solution was then evaporated, and left 17·58 per cent of a brown transparent extract, (Gmelin's *coffee-bitter*,) soluble in water, and having the characteristic bitter taste of the raw coffee bean. It is insoluble in ether and in absolute alcohol, and sparingly soluble in alcohol of 0·84, but its aqueous solution is not precipitated by alcohol. It is not altered by dilute acids or alkalis; the last deepen its colour, and lime water precipitates it of a green colour: the salts of iron produce with it a grass green colour, and a dark green precipitate falls, soluble in excess of acid. When an alkali is added to its solution, previously mixed with a salt of copper, a fine green precipitate falls, which, carefully prepared without excess of oxide of copper, may be used as a pigment. Acetate of lead precipitates it yellow green, and protochloride of tin, gray; and when these precipitates are decomposed by sulphuretted hydrogen, the extractive is evolved unchanged. It is neither precipitated by gelatine nor by infusion of galls. It yields ammonia on destructive distillation, and a crystallized sublimate.

The substance precipitated by the addition of alcohol to the original decoction of the coffee, was a mixture of 3·6 per cent. of brown gum, and 37 pulverulent extractive. The coffee beans also contain resin, and a fat oil, which may be extracted by alcohol. The insoluble residue constituted two thirds of the weight of the beans. When burned, coffee beans leave 4 per cent. of ash, consisting of carbonate of potassa, (the base of which was combined with a vegetable acid,) sulphate of potassa, chloride of potassium, carbonate and phosphate of lime, magnesia, and the oxides of iron and manganese.

The crystallized sublimate alluded to by Schrader has since become the subject of separate examination; it is the *caffein* of Pelletier and others, and was first obtained by Runge in 1820. There are various methods of obtaining it, and it may be procured in considerable quantity by those who roast large quantities of coffee; it sublimes in a very impure form, but is easily deprived of its adhering impurities. The process generally recommended for its preparation is that of Runge; it consists in making a strong aqueous infusion of ground raw coffee, adding to it a solution of sugar of lead, which occasions a green precipitate, and

leaves the supernatant liquor colourless; the excess of the salt of lead in this liquor is then precipitated by sulphuretted hydrogen, it is filtered, and evaporated; the caffeine remains, and must be treated by animal charcoal to whiten it, and recrystallized.

Caffein forms white silky crystals, soluble in boiling water and alcohol, and deposited in crystalline filaments as these solutions cool; it has no alkaline reaction, nor does it saturate acids; it is, therefore, not an alkaloid; yet it resembles those bodies in ultimate composition, consisting, according to Pfaff and Liebig (*Ann. de Ch. et Ph.*, xlix. 303), of

Carbon . . .	8 . . .	48 . . .	49.5
Hydrogen . . .	5 . . .	5 . . .	5.1
Oxygen . . .	2 . . .	16 . . .	16.5
Nitrogen . . .	2 . . .	28 . . .	28.9
Caffein	1	97	100.0

Roasted Coffee.—According to Cadet (*Ann. de Ch.*, lviii.), coffee roasted to a pale brown colour loses 12.3 per cent.; to a chestnut brown, 18.5 per cent., and to a black, 23.7 per cent. So that the loss of weight in coffee roasting may be estimated at about 12 to 20 per cent. Schrader found, in roasted coffee,

Extractive matter soluble in water and alcohol, closely resembling that of raw coffee, but browner and deliquescent	12.5
Brown gum	10.4
Extractive, soluble in water, but insoluble in alcohol	5.7
Oil and resin	2.0
Insoluble burned woody fibre	69.0
	99.6

When roasted coffee was distilled with water, the aroma passed over; the distilled water reddened litmus, and had the agreeable odour of the coffee. When raw coffee is so roasted as to collect the volatile products, a portion of fragrant empyreumatic oil passes over, which, in the ordinary mode of roasting, is lost. According to Chevenix, (*Tillock's Magazine*, xii. 350.) a portion of tannin is formed during roasting; and Cadet states, that the greatest proportion of tannin is contained in slowly and slightly-roasted coffee, and that, when it is very brown or black, its proportion is much diminished. This product, however, probably depends much upon temperature, for Payssé, Schrader, and Runge, assert that gelatine is not precipitated by an infusion of roasted coffee. Schrader endeavoured to ascertain the particular principle to which the flavour and aroma of roasted coffee are due, by exposing each of the proximate principles of unroasted coffee separately to heat; but he found that no one of them yielded any peculiar flavour, and that the ligneous residue, when roasted, acquired as much of the characteristic flavour as when the other principles were retained; so that the flavour of roasted coffee must be ascribed to the joint effect upon all the constituents: the caffeine seems to play a very passive part as far as flavour is concerned, and a considerable proportion of it remains unchanged after roasting, whilst another part of it is merely volatilized.

The flavour of coffee as a beverage depends, in the first place, upon the *roasting*, and, in the next, upon the mode of *making* the infusion; the coffee should be rapidly but well roasted, and it is said to be improved by

roasting it in a close vessel; it should be aired and ground into fine powder immediately before use; it is sometimes *boiled*, and sometimes *infused*; in the former case, the coffee is darker coloured, more bitter, and has more of an acid flavour than when infused, and the infusion in a close vessel is more aromatic than that in an open one, especially when the coffee-pot is so managed as to *steam* the powder. The pleasantest flavour is obtained by placing a *sufficient quantity* of finely-ground and freshly-roasted coffee upon a filter, (very coarse filtering paper in a funnel answers very well,) and pouring boiling water upon it so as to filter quickly into the vessel beneath. When coffee is made by boiling it is apt to be thick, unless fined by the addition of a little white of egg, or isinglass, which probably carries down the tannin. In *Parker's Coffee Fountain*, a stream of boiling water is forced through a cylindrical vessel containing the ground coffee, by the pressure of steam; it affords excellent coffee, when properly managed.

7. CATHARTIN.—Lassaigne and Feneulle, in their analysis of *senna-leaves* (*Jour. de Phar.*, x. 59), obtained from them a little volatile oil, having the nauseous odour of the infusion of senna. A cold infusion of senna contains vegetable albumen. From a decoction of senna precipitated by acetate of lead, decomposed by sulphuretted hydrogen, and subjected to the action of several other solvents, they obtained a bitter purgative principle, which they called *cathartine*; but, from the complexity of the process, it seems doubtful how far the product is to be regarded as a real proximate principle of senna: the whole subject requires revision. The effects of various reagents upon an infusion of senna, are detailed by Mr. Batley in the *London Medical Repository*. (xv. 169.)

8. COLOCYNTIN, or the purgative principle of the pith of colocynthida, was extracted by Vauquelin from that substance by the action of alcohol, which left on evaporation a resin-like matter, difficultly-soluble in water, readily soluble in alcohol, and in acids and alkalis, and eminently bitter and purgative.

9. ELATIN.—The fruit of the *wild cucumber* (*Cucumis elaterium*) furnishes a very acrid juice, which deposits the powerful cathartic known under the name of *elaterium*. This substance occurs in commerce in thin cakes of a greenish colour and bitter taste; it derives its cathartic powers from a small portion of a very active principle, which Dr. Paris has called *Elatin*. (*Pharmacologia*.) From 10 grains of elaterium, he obtained,

Water	0.4
Extractive	2.6
Fecula	2.8
Gluten	0.5
Woody matter	2.5
Elatin	1.2
Bitter principle	

10.0

By boiling elaterium in alcohol, distilling off the greater part of the solvent, and setting the remainder aside to evaporate spontaneously, Mr. Hennell obtained a *green resin*, in which the purgative quality resides, and a crystallized substance; he separated these by the action of ether,

which took up the resin and left the crystallized product; the latter was purified by solution in hot alcohol and crystallization: it was nearly insoluble in water and in ether, but soluble in hot alcohol, bitter, fusible at about 350°, neither acid nor alkaline, and composed of 36.9 carbon, 23.9 hydrogen, and 39.2 oxygen per cent. In elaterium, Hennell found 40 per cent. of the crystallizable matter, and 21 of the purgative resin, the residue being lignin, starch, and earthy matter. (*Jour. R. Inst.*, N.S., i. 532.)

10. RHABARBARIN.—The purgative principle of rhubarb is stated by Nani, of Milan, to be an alkaloid, but the details of his experiments have not been given. (*Quart. Jour.*, xvi. 172.)

The root of rhubarb (*Rheum palmatum*), as it occurs in commerce, has been examined by Schrader and myself with the following results.

Water	8.2	Resin	2.8
Gum	31.0	Rhabarbarin	24.0
Resin	10.0	Mucilage	14.8
Extract, Tan, and Gallic acid	26.0	Woody fibre	47.0
Phosphate of lime	2.0	Oxalate of lime	9.0
Malate of lime	6.5	Loss	2.4
Woody fibre	16.3		

(SCHRADER, *Gmelin's Handb.*) 100.0

(BRANDE, *Quar. Jour.*, x. 291) 100.0

11. RHEIN.—When 1 part of powdered rhubarb is gently heated with 8 of nitric acid, specific gravity 1.37, and the liquor evaporated to the consistence of syrup, and diluted with cold water, an orange-coloured powder is deposited, which M. Vaudin has termed *Rhein*; it is inodorous, bitter, sparingly soluble in cold water, soluble in alcohol, ether, and boiling water, reddened by the alkalis, and rendered paler by the acids. It is stated not to be a *product*, but to pre-exist in rhubarb, and to be extracted from the root by ether: it requires re-examination.

12. RHAPONTICIN is a substance obtained from the *Rheum rhaponticum*, in the form of yellow scales, inodorous, insipid, and insoluble in cold water; soluble in 24 parts of boiling water, and in 2 of anhydrous alcohol. (HORNEMANN.)

13. GENTIANIN.—This principle has been extracted by the following process from the root of the *Gentiana lutea**, by Henry and Caventou. (MAJENDIE'S *Formulary*, translated by Gregory.)

“Treat powdered gentian with cold ether, which in forty-eight hours

* Many other bitter substances have been described as distinct *proximate principles*, but their title to that character is so doubtful, that I have here omitted their enumeration. They generally partake of the above-described characters either of gum, resin, or extractive. *Hops* contain a bitter extractive matter, which has been termed *lupulin*, a name first applied by Dr. Ives, of New York, to the pollen, or *condition* of the hop, which consists of 36 resin, 12 wax, 11 bitter extract or *lupulin*, 5 tannin, 10 extractive insoluble in alcohol, and 46 insoluble residue. (See also PAYEN and

CHEVALLIER, *Jour. de Pharm.*, viii. 216.) Some of these bitters have been alluded to above.

Bryonin, obtained by Vanquelin and Brandes from the *Bryonia alba*; *cytisin*, from the *Cytisus laburnum*, by Chevallier and Lassaigne; *scillitin*, from the *Scilla maritima*, by Vogel; *senegin*, from the *Polygala senega*, by Gehlen; *saponin*, from the *Saponaria officinalis*; *guaranin*, from the fruit of the *Paullinia sorbilis*, by Martius; *Columbin*, from *Calumba root*, are a few of the active principles of plants which have been regarded as distinct proximate components. Among the in-

furnishes a greenish yellow tincture; this being filtered, poured into an open vessel, and exposed to heat, passes on cooling, (if the liquor be sufficiently concentrated,) into a yellow crystalline mass, with the odour and taste of gentian very powerfully developed. This mass is to be treated with alcohol, until it ceases to yield a citron colour. The washings are then to be united and exposed to a strong heat, when the crystalline substance reappears and concretes towards the close of the evaporation into a mass which is exceedingly bitter. This, taken up again by weak alcohol, is dissolved, with the exception of a certain quantity of oily matter. The last spirituous solution, besides the bitter principle of gentian, contains an acid substance and the odorous matter also.

“By evaporating this liquid to dryness, washing the residue in water, adding a little calcined and well-washed magnesia, boiling, and evaporating in a water bath, the greater part of the odorous matter of the gentian is dispersed, the acidity is removed by the magnesia, and the bitter principle remains partly free and partly combined with the magnesia, to which it imparts a fine yellow colour. On boiling this magnesia with ether, the greater part of the bitter principle is obtained, which may be isolated and rendered pure by evaporation. If it be desired to separate the greater part of the bitter principle that remains in the magnesia in a fixed state, and which could not be taken up by the ether, we may treat it with oxalic acid in sufficient quantity to produce slight acidity. The acid seizes upon the magnesia, and sets the bitter principle at liberty, which may be recovered in the manner already described.

“Gentianin is yellow, inodorous, possessing in a powerful degree the aromatic bitter taste of gentian, which is very much increased by solution in an acid. It is very soluble in ether and alcohol, and separates by spontaneous evaporation under the form of delicate crystalline needles of a yellow colour. It is much less soluble in cold water, which it renders notwithstanding very bitter; boiling water more readily dissolves it. Diluted alkalis heighten its colour very much, and dissolve a little more of it than water. Acids diminish its yellow colour in a very remarkable manner. With sulphuric and phosphoric acids the solution is almost colourless; but with the weaker acids, such as acetic, it is still yellowish. Concentrated sulphuric acid carbonizes it and destroys its bitterness. Exposed in a glass tube to the heat of boiling mercury, gentianine sublimes in the form of small yellow crystalline needles, and is partially decomposed. It has no sensible effect on turnsole, either when blue or reddened by acids. It is apparently neutral.”

14. THEIN.—According to Oudry, *tea leaves* contain a peculiar principle, (salifiable base?) which he says may be separated as follows (BERZELIUS, *Lehrbuch*, iv.): 12 parts of tea were infused for twenty-four hours in 200 of cold water, in which 3 of common salt were dissolved. The infusion was evaporated to dryness, and the residue digested in alcohol of

vestigations of this kind, those relating to *sarsaparilla* seem to hold out promising results, for there are peculiarities belonging both to the chemical and medical properties of the root, which will probably be traced to a distinct substance. The

parillin and *smilacin* of Pallotta and Folchi I have not been able to identify. The systems of Berzelius and Gmelin may be consulted for abstracts of what is known upon the above subjects.

0.81; the residue of this alcoholic tincture was then dissolved in water, and digested with magnesia, and filtered. On evaporating the filtered liquor to a certain degree of concentration, crystals of *thein* were obtained, and the magnesian residue, digested in alcohol, yielded a further portion.

Thein requires 30 to 40 parts of water at 50° for solution, and crystallizes irregularly on evaporation. When heated, it first fuses and is then decomposed. It has no alkaline properties to tests, but it forms crystallizable compounds with sulphuric and with citric acid. Berzelius observes that these statements require corroboration.

Some years ago I examined the varieties of tea in common use (*Quarterly Journal*, xii. 201), and found that the quantity of astringent matter precipitable by gelatine is somewhat greater in *green* than in *black tea*, though the excess is by no means so great as the comparative flavours of the two would lead one to expect. The entire quantity of soluble matter is also greater in *green* than in *black tea*, but the extractive matter not precipitable by gelatine is greater in the latter.

The following table shows the respective quantities of soluble matter in water and in alcohol, the weight of the precipitate by isinglass, and the proportion of inert woody fibre in green and black tea of various prices. It is given, not as throwing any important light upon the cause of the different qualities and effects of tea, but as containing the results of actual experiments. It will be remarked, that when tea-leaves have been exhausted by water repeatedly affused, alcohol is still capable of extracting a considerable quantity of soluble matter: the alcoholic extract, infused in boiling water, furnishes a liquid which smells and tastes strongly of tea, and which, were it not for the expense of the solvent, and the trouble attending its separation, might perhaps be profitably employed.

One hundred parts of Tea.		Soluble in Water.	Soluble in Alcohol.	Precipitate with Jelly.	Inert Residue.
Green Hyson	14s. per lb.	41	44	31	56
"	12s. "	34	43	29	57
"	10s. "	36	43	26	57
"	8s. "	36	42	25	58
"	7s. "	31	41	24	57
Black Souchong	12s. "	35	36	28	64
"	10s. "	34	37	28	63
"	8s. "	37	35	28	63
"	7s. "	36	35	24	64
"	6s. "	35	31	23	65

§ XX. PARTS OF PLANTS.

I SHALL include in this section a short notice of the chemical components of some of the *parts of plants* useful in medicine and the arts, and which I have not elsewhere noticed. The third volume of BERZELIUS' *Lehrbuch* (German or French translation), and the article on *Chemical Botany* in LEOPOLD GMELIN'S *Handbuch* (vol. iv.), may be referred to for further details.

1. ROOTS.—*Allium sativum*, and *Allium cepa*. Garlic and onions have been but imperfectly examined. They both yield, on pressure, a juice strongly odorous, and which reddens on exposure to air, and is acid; they yield a volatile oil on distillation, and onions afford *mannite* (p. 1082).

Anomum curcuma, or *Curcuma longa*. Turmeric root, as a colouring material, has been above noticed (p. 1118). It contains, according to John, 1 yellow volatile oil, 12 resin like gamboge, 14 gum, 57 lignin. Turmeric is cultivated in the East Indies, and used as a condiment, especially in *Curry powder*. Digested in water or alcohol, it furnishes a large proportion of yellow colouring matter. Most of the acids render it paler, and the alkalis change it to a deep brick-red; hence its use as a test of the presence of alkaline matter. It is also reddened by boracic acid, and by hydrochloric acid gas. Some of the peculiarities of the colouring principle of turmeric have been noticed by M. Desfosses (*Ann. de Ch. et Ph.*, xvi. 75), and by Mr. Faraday (*Quar. Jour.*, xi. 403).

Anomum zinziber. (BUCHOLZ.) Ginger root contains 1·56 volatile oil, 3·6 acrid resin, 10·5 acrid and sourish extractive, 12·5 gum, 19·75 starch? 8·3 mucilage, 26 extractive, 8 lignin, remainder water and loss.

Angelica archangelica. Essential oil and fragrant aromatic resin 6·7, bitter extract 12·5, gum 33·5, inulin 4, matter soluble in alkali 7·3, lignin 30, water and loss 6. (JOHN.)

Anthemis pyrethrum. The stimulating power of this root upon the salivary glands is due to its soft resin. It contains traces of volatile oil, soft resin 5, yellow extractive 14, gum 11, inulin 33, lignin 35. (GAUTIER.)

Aristolochia serpentaria. Volatile oil 0·5, yellow soft resin 2·85, extractive 1·70, saponaceous gum 18·10, lignin 62·4, water and loss 14·5. (BUCHOLZ.)

Asarum europæum. In the root Lassaigue and Feneulle found a crystallizable volatile oil, somewhat resembling camphor. It has been called *asarin*.

Aspidium filix mas. Male fern-root contains, according to Morin, a trace of volatile oil, fat oil, sugar, starch, tannin, pectine, malic and gallic acids combined with lime and potassa, phosphate of lime, and lignin; its ashes yielded silica, alumina, and oxide of iron.

Berberis vulgaris. The root yielded 2·55 of brown colouring matter, precipitable by acetate of lead; 6·62 of a fine yellow extract (*dye-stuff*), not so thrown down; gum 0·35, starch 0·2, oil 0·4, soft resin 0·55, lignin 55·4, water, earthy and alkaline salts, &c., 35.

Beta vulgaris. Common beet-root. (See pp. 1081 and 1098.)

Brassica rapa. Turnips. (See p. 1098.)

Bryonia alba. Bryonin has been above adverted to. According to Brandes and Firnhaber the root contains, bryonin and a little sugar 1·9, resin and a little wax 3·4, mucilage, gum, starch, and pectine 29·4, albumen 6·5, extractive 1·7, lignin 15·25, water 20.

Calicocca, or *Cephaelis ipecacuanha*. Ipecacuanha root has been examined by MM. Pelletier and Majendie, and an account of their researches is published by M. Robiquet, in the *Ann. de Ch. et Ph.*, iv. 172. 100 parts of this root, deprived of the woody fibre which traverses its centre, afforded, fatty matter 2, emetina 14, gum 16, starch 18, woody fibre 48, a trace of wax, loss 2. The means of separating the *emetic principle* have already been described. (See p. 1231.)

Cichorium intibus. Succory-root is much used in Germany and elsewhere, when roasted, as a substitute for coffee: it has not been satisfac-

torily analyzed. According to Juch it contains 0.25 bitter extractive, 0.03 resin, traces of sugar, and the rest lignin.

Cochlearia armoracia. *Horseradish.* Einhof obtained from 4 pounds of the fresh root, 3 lbs. 2 oz. water, 20 grs. volatile oil, 31.5 grs. albumen, 1.5 oz. and 20 grs. of starch, 1.5 oz. of gum and sugar, 6 grs. bitter resin, 1 drachm 41 grs. acetate of lime, sulphate of lime, and acetic acid, 8 oz. lignin.

Colchicum autumnale. (See *Veratria*, p. 1223.) The bulbs contain a fatty matter resembling that of veratria, and of sabadilla seed? also gum, inulin, starch, extractive, gallate of veratria, and lignin. 100 lbs. of the recent bulbs yield between 18 and 19 lbs. of *pharmaceutical extract*.

Columbo. The supposed existence of a distinct principle in this root has been adverted to; it contains, according to Planche, one third its weight of starch, and a peculiar nitrogenous principle, to which the tendency of its infusion to putrify is ascribed; also a peculiar yellow bitter, not thrown down by metallic salts, and soluble in water and alcohol, to which its medical virtues are due: one third its weight is lignin. The average produce of *pharmaceutical extract of columbo* is 62 per cent.

Convolvulus jalappa. *Jalap*, analyzed by Cadet de Gassicourt, yielded 10 resin, 5 starch and albumen, 44 gummy extract, 28 lignin, exclusive of salts, water, and loss. The supposed existence of *jalapin* has, I believe, not been verified. The average produce of *pharmaceutical extract of jalap* (*Lond. Phar.*) is 66 per cent.

Crameria triandra. *Rhatany root.* 38.3 tannin, 6.7 sweet extractive, 2.5 azotized mucilage, 8.3 starch, 43.3 lignin.

Daucus carota. Carrots have been mentioned as a source of sugar and pectine (pp. 1071 and 1098). Hermbstadt obtained 6½ lbs. of syrup from 124 lbs. of carrots.

Gentiana lutea. (See p. 1239.) According to Henry (*Ann. of Phil.*, xvi. 98), gentian contains the following substances: 1. a substance resembling bird-lime; 2. a resin combined with oil, which gives to gentian its peculiar odour; 3. a bitter extractive principle; 4. gum and colouring matter; 5. phosphate of lime? 100 lbs. of gentian root yield about 62 of *pharmaceutical extract*.

Glycyrrhiza glabra. Two of the compounds of *liquorice root* have already been mentioned, namely, a peculiar *sugar*, and *asparagin* (pp. 1083 and 1234). Robiquet found in it the following substances (*Ann. de Ch.*, lxx.): 1. starch; 2. gluten; 3. liquorice sugar; 4. phosphate and malate of lime and magnesia; 5. an acrid oil; 6. a crystallizable substance resembling asparagin; 7. woody fibre.

Inula helenium. (See *Inulin*, p. 1090.) Elecampane root contains, volatile oil 0.4, wax 0.6, acrid soft resin 1.7, bitter extractive soluble in alcohol and water 36.7, gum 4.5, inulin 36.7, albuminous matter 13.9, lignin 5.5. (JOHN.) By the action of alcohol on the dried root a crystallizable substance is separated, which has been termed *Hellenin*, described and analyzed by Gerhardt. (*Ann. de Ch. et Ph.*, lxxii. 163.)

Leontodon taraxacum. Dandelion root is stated by John to contain in its milky juice a portion of caoutchouc, besides sugar and gum, and a very small quantity of bitter extractive. 100 lbs. of the fresh root yield 11 lbs. of *pharmaceutical extract*. Mr. Squires' experiments upon this

root show that its expressed juice contains gum, albumen, gluten, an odorous principle, extractive, and a crystallizable bitter principle. (BRANDE'S *Dictionary of Pharmacy*, 532.)

Marantha arundinacea. The root of this plant has been mentioned as a source of the species of starch which we call *arrow root*. The fresh root contains, according to Benzoin, volatile oil 0·7, starch 26, albumen 1·58, gummy extract 0·6, lignin 6, water 65·6.

Orchis mascula. The root, called *salep*, contains *starch* and *mucilage*.

Pastinaca sativa. From 124 lbs. of parsneps Hermbstadt obtained $5\frac{1}{2}$ lbs. of syrup: according to Drapier they yield (when dried?) 12 per cent. of sugar.

Polygala senega. Senega root yields 7·5 soft resin, 6·15 *senegin*, 26·85 extractive, 9·5 gum and albumen, 46 lignin.

Rheum palmatum. (See p. 1239.) 100 lbs. of Indian rhubarb yielded 69 lbs. of aqueous extract.

Rubia tinctorum. *Madder root* is an article of great importance in *dyeing*; it grows wild in most parts of the south of Europe, and is largely cultivated in some parts of Holland and the Levant; its red colour is apt to be injured by drying, a process requiring much caution. Good madder has a strong and peculiar smell; it exhibits, when cut, a cortical and a woody part of a red colour, intermixed in the former with yellow spots. The red portion is most soluble. A peculiar substance, obtained from madder, has already been noticed under the name of *Alyzarine*. (See p. 1112.)

Scorzonera hispanica. The fresh root of this plant contains, 9 starch, 3 resin, 10 extractive, 32 water, 46 lignin. (JUCH.)

Smilax sarsaparilla. The varieties and uses of this root I have described in the *Dictionary of Pharmacy*. (See also p. 1241, *note*.) Canno-bio's analysis is as follows: acrid bitter resin 2·8, gummy extract 5·5, starch 54·2, lignin 27·8, loss 9·7. The relative quantity of starch compared with that of extractive is enormously great in some species as compared with others. The average produce of the *red sarsaparilla* in *pharmaceutical extract* is 33 per cent.

Solanum tuberosum. For the analysis of *potatoes*, see p. 1084, *note*.

Triticum repens. The root of this species of grass abounds in sugar; 100 parts of dry root (= 112 fresh) yield 17 to 18 parts of an agreeable syrup, (*Mellago graminis* of foreign pharmacy.) Pfaff has rendered it probable that it contains *manna sugar*.

Valeriana officinalis. This root contains, according to Trommsdorf, volatile oil 1·2, a peculiar extractive, including the acid? 12·5, gum 18·75, an odorous soft resin 6·25. The essential oil is the seat of the odour. 100 lbs. of clean valerian root yield between 38 and 39 of *pharmaceutical extract*. Trommsdorf has discovered a peculiar acid in this root, which he called *Valerianic acid*. (*Ann. de Ch. et Ph.*, Liv. 208.) It goes over along with water and oil when Valerian roots are distilled with water; it is a colourless limpid liquid having the odour of the essential oil of the plant. The *Valerianates* are described in the above-quoted paper. (See also p. 1264, *note*.)

Veratrum album. See *veratria* (p. 1223). The root contains a peculiar fatty matter, yellow extract, gallate of veratria, gum, starch, and lignin.

2. BARKS.—*Æsculus hippocastanum*. The bark of the *horse-chestnut* has been partially examined by M. Henry. (*Ann. de Ch.*, LXXVII.) It appears to contain scarcely any resin; water and diluted alcohol dissolve nearly the whole of its soluble contents, which are chiefly extractive and mucilage. Tincture of galls does not render its infusion turbid; it does not contain an alkaloid. According to Pelletier and Caventou, this bark contains a green fixed oil, a red resin, a red extract, a yellow bitter extract, tannin, gum, and a free acid. (See *esculic acid*, p. 1142, *note*.)

Brucea antidysenterica. The bark of this tree is in fact *angustura bark* (*Bonplandia trifoliata*), and not the *spurious angustura*, which is the bark of a *strychnos*. (See p. 1221.) *Angustura bark* (*cusparia bark* of our Pharmacopœia), contains, according to Fischer, acrid volatile oil 0·3, bitter hard resin 1·7, balsamic soft resin 1·9, bitter extractive, with a trace of caoutchouc, 3·7, gum 5·7, lignin 89·1.

Cinchona lancifolia, *cordifolia*, and *oblongifolia*, and other species. (See *cinchonia*, *quinia*, &c.) The varieties of Peruvian bark have been examined by MM. Pelletier and Caventou. In the *Cinchona lancifolia*, or *pale bark*, they found the following constituent parts: 1. *Cinchonia*, combined with kinic acid; 2. green fatty matter; 3. red and yellow colouring matter; 4. tannin; 5. kinate of lime; 6. gum; 7. starch; 8. lignin.

In *yellow bark* they found, 1. *quinia*, with kinic acid; 2. yellow fatty matter; 3. yellow colouring matter; 4. tannin; 5. kinate of lime; 6. starch; 7. lignin. In *red bark* the same substances as in the two former. There can be no doubt that the tannin, and probably the colouring extractives, as well as the alkaloids and the kinic acid, all contribute to the medical efficacy of these barks. The produce in *pharmaceutical extract*, of *pale bark*, is about 36 per cent. (See p. 1210.)

Croton cascarilla. This bark, analyzed by Trommsdorf, gave 1·6 volatile oil, 15·5 bitter soft resin, 18·7 bitter gummy extractive, 65·6 lignin. 100 lbs. of *cascaquilla bark* yield about 30 of *pharmaceutical extract*.

Daphne Mezereon. Gmelin and Bär obtained from *mezereon bark*, daphnin (p. 1235), wax, acrid resin, yellow colouring matter, a saccharine and brown extract, gum, malic acid, lignin, and several salts. (See BERZELIUS, for details.)

Laurus Cassia. The bark contains volatile oil 0·8, tasteless pale brown soft resin 4, gummy extract 14·6, lignin 64·3, water and loss 16·3. (BUCHOLZ.)

Laurus cinnamomum. The finest Ceylon cinnamon bark yields essential oil, a soft aromatic resin soluble in ether, tannin, extractive, gum, and above 80 per cent. of lignin. (VAUQUELIN.) Dumas and Peligot have ascertained that the crystals deposited by this oil and by oil of cassia are not benzoic acid, but a peculiar acid product arising apparently out of the oxygenation of the oil; they have called it *cinnamic* or *cinnamomic acid*. (See p. 1157.)

Pinus sylvestris. The inner bark of the young Scotch fir was, for many years, used by Westring in the cure of intermittents. Berzelius found in it soft resin 6·9, tannin with extractive 6·65, a bitter extractive, precipitable by subacetate of lead, and containing sugar, 15·0, cinchonate

of lime 0.53, a gelatinizing principle 18.15, water and loss 5.25. Berzelius considers the gelatinizing matter to be pectic acid and starch; and hence the nutritive property of this bark, which induces the peasantry in northern countries to use it as a substitute for bread in years of scarcity. (See p. 1096.) The soft resin is turpentine?

Quassia simarouba. The bark, used in medicine, contains a volatile oil, bitter extract, traces of gallic acid, and many salts.

Quercus robur. Oak bark. (See p. 1102.) 100 lbs. of oak bark yield, on an average, 20 lbs. of aqueous extract.

Ulmus campestris. Elm bark contains a green fatty matter, soluble in alcohol and ether; it is obtained by the action of water upon the alcoholic extract of elm bark, which leaves it soluble in ether. This bark also contains a peculiar gelatinous matter (a salt of pectine?) A peculiar and modified extractive oozes from elm bark, which I have above described under the name of *ulmin*. Berzelius justly inveighs against the application of that term to a variety of dissimilar products.

Wintera aromatica or *Winter's canella bark*. It contains an acrid volatile oil, mild resin, coloured extractive, a peculiar kind of extractive and of sugar, gum, starch, albumen, lignin, and several salts. (HENRY, PETROZ, and ROBINET.)

Zanthoxylum caribæum. (*Z. clava Herculis*.) The bark of this tree is used in the Antilles as a febrifuge; Chevallier and Pelletier found in it a peculiar principle, which they termed *zanthopicrite*. It is soluble in water, very soluble in alcohol, insoluble in ether; it forms yellow silky crystals, and is very bitter and astringent; it has no alkaline reaction; animal charcoal extracts it from its aqueous solution, and hot alcohol extracts it again from the charcoal. (*Jour. de Chim. Med.*, ii. 314.)

3. WOODS.—*Cæsalpinia crista.* *Fernambuc* or *Brazil wood*. *Peach wood?* (See p. 1113.) This tree grows in Brazil, in the Isle of France, Japan, and other countries: the wood is hard and heavy, and though pale when recent, it acquires a deep-red colour by exposure. Digested in water, it affords a fine-red infusion, of a sweetish flavour: the residue, which appears nearly black, imparts much of colour to alkaline liquors. With alcohol, it gives a deep-red tincture; alkalis and soap convert its red colour to a fine purple: hence paper, tinged with Brazil wood, is sometimes used as a test for alkalis; acids render it yellow; alum produces a fine crimson lake with infusion of Brazil wood; chloride of tin forms with it a crimson precipitate, bordering on purple; the salts of iron give a dingy purple colour. Sulphuretted hydrogen destroys the colour of infusion of Brazil wood, but it re-appears on expelling the gas. (CHEVREUL, *Annales de Chimie*, LXvi.)

Guaiacum officinale. *Lignum vitæ.* Hagen obtained 3 per cent. of resin of *guaiacum* (p. 1157, note) from this wood. From 1 ounce of rasped wood Trommsdorf obtained (in different samples) from 35 to 160 grains of matter soluble in alcohol, and from 45 to 96 grains of watery extract. When *guaiacum* wood is boiled in water, a small part of the resin is dissolved; the residue becomes blue by exposure to air. (*Phil. Trans.*, 1811.)

Hæmatoxylon campechianum. *Logwood.* (See *dye-stuffs*, p. 1113.)

This wood imparts a fine purple or crimson colour to pure water, but its tint is altered by the slightest metallic impregnation; alkalis deepen it, and acids render it paler; alum forms with it a violet-coloured lake; sulphate of iron renders the infusion of logwood deep purple, or nearly black; sulphate of copper and acetate of lead throw down brown and purple precipitates; and hydrochlorate of tin precipitates the whole of the colouring matter in the form of a purple compound. Many of the colours which logwood produces are not very durable. (BANCROFT, on *Permanent Colours*, ii. 338; CHEVREUL, *Annales de Chimie*, LXvi. 254.) 100 lbs. of logwood yield 25 lbs. of *pharmaceutical extract*.

Morus tinctoria. (See p. 1117.)

Pterocarpus santalinus. This tree, which affords *saunders* or *red sandal wood*, is a native of several parts of India. Its deep-red colouring matter is insoluble in water, but readily soluble in alcohol; it is chiefly employed for colouring a few pharmaceutical tinctures. The insolubility of its colouring principle in water furnishes a ready mode of distinguishing between it and *Brazil wood*; and its solubility in alcohol renders it probable that it is of a resinous nature. (See p. 1114.)

Quassia excelsa. The wood of this tree, which has long been used in medicine as a powerful bitter, has not been minutely examined; it is said to contain a slight trace of volatile oil, a peculiar bitter extractive (*quassin*), gum, lignin, and salts. The bitter extractive is much more soluble in common alcohol than in water. It is precipitated, according to Pfaff, by acetate of lead: its aqueous solution, sweetened, is a good *fly-poison*.

Solanum dulcamara. The stalks of this plant contain, according to Pfaff (*Mat. Med.*), 21 per cent. of a saccharo-bitter extract, which he terms *Picroglycion*. Its bitterness is derived from *malate of solania* (p. 1225).

Strychnos columbina. *Snakewood*. It contains green fat, yellow extractive, gum, strychnate or igasurate of strychnia (p. 1219), and lignin.

4. HERBS. FUNGI. LICHENS.—*Anemone pulsatilla* and *nemorosa*. The concentrated distilled water of this plant, when kept for some weeks in a cool place, deposits a crystalline matter, originally described by Heyer, and afterwards by Vauquelin and Robert. (*Jour. de Phar.*, vi. 229.) It passes over with the vapour of water, and appears at first as an oil, which afterwards concretes. Its vapour is acrid, and the substance itself, poisonous. It burns like camphor, is very sparingly soluble in water, and decomposed by concentrated acids and alkalis. It has been termed *anemonin*, and *anemone camphor*.

Many other plants, especially many species of *ranunculus*, *clematis*, and *rhus*, and the *arum maculatum*, and *polygonum hydropiper*, contain an acrid principle analogous to, and by some considered identical with the above.

Artemisia absinthium. *Wormwood* has not been examined by modern chemists. According to Dörffurt, dry wormwood yields about 1 per cent. of volatile oil, 8.5 to 9 of green resin, 25 to 30 of gummy extract, which, when burned, leaves 11.5 per cent. of the original weight of the dried herb, of ashes, two thirds of which are carbonate of potassa: hence the

term *salt of wormwood* applied to that salt. According to Kunsemüller, the potassa in the herb is in a state of *acetate*.

Agaricus, &c. See Braconnot's researches, already quoted, (*Fungic and boletic acid, sugar, fungin*.) The substances found in all *fungi* are a crystalline and a butyraceous fat, albumen, sugar, two azotized bodies, one of which is only soluble in water, and the other in water and alcohol, and salts of potassa and of ammonia, with fungic, boletic, phosphoric, and sometimes acetic acid, fungin (a form of lignin), and water. Many contain gum and mucilage.

When bruised fungi are digested in water, they yield an *extract*, from which alcohol abstracts sugar and an azotized substance, separable by a little alcohol, which dissolves the former and leaves the latter. This azotized substance yields a brown solution with water, which, when evaporated, leaves it in the form of a brown extract, smelling, when heated, like roasted meat, evolving ammonia when distilled, and in all respects resembling the animal extractive called *osmazome*. The portion of the extract, insoluble in alcohol, dissolves in water, with the exception of a little albumen. It also dissolves in dilute alcohol: it does not gelatinize, and when destructively distilled, yields carbonate of ammonia.

The insoluble portion of the fungi, which remains after digestion in water, digested in alcohol, yields stearin and elain, and a little resin.

Chemical analysis has not thrown any light upon the *poisonous* nature of certain mushrooms.

Asparagus officinalis. The juice of *asparagus*, in the state in which it comes to table, yields, as already stated (p. 1234), a very curious product, which has been termed *asparagin*; it also contains a little albumen, wax, and resin. The residue of the asparagus, which contains its eatable part, for boiling probably abstracts the matters contained in its expressed juice, has not been examined; nor have we any accurate information as to the cause of the singular odour which it imparts to the urine: it has been said, however, that *asparagin* is diuretic, and gives the urine the same odour.

Boletus juglandis, laricis, and *pseudo-ignarius*, have been examined by Braconnot. (*Ann. de Chim.*, LXXX. 273.)

Brassica oleracea. Cabbage. The fresh leaves yield, per cent. 0.63 green fecula, 0.29 albumen, 0.05 resin, 2.89 gum or mucilaginous extract, 2.84 extract soluble both in alcohol and water. The saline matters are sulphate and nitrate of potassa, chloride of potassium, malate and phosphate of lime, phosphate of magnesia, and oxides of iron and manganese. (SCHRADER.) So that, according to this analysis, the cabbage may be assumed to contain about 7 per cent. of soluble matter, the remainder being lignin and water.

Cetraria islandica. *Lichen islandicus*. Iceland moss has been somewhat minutely examined by Berzelius; the details of his analysis are given in his *Lehrbuch*. The result is, green-wax 1.6, yellow colouring extractive 7.0, bitter principle 3.0, sugar 3.6, gum 3.7, starch 44.6, starchy lignin 36.2; a trace of gallic acid, tartar, tartrate of lime, and phosphate of lime 1.9. It has also been analyzed by John, with the following results: green resin 1.5, extractive 10, inulin 8.0, modified inulin 40.0, insoluble parts 37.5, saline substances 3.0.

Cochlearia officinalis. The extract of the expressed juice contains brown sweet extract, soluble in hot alcohol, and precipitable by chlorine and by tannin, 48·33: matter insoluble in alcohol, but precipitable by tannin, 32·00, salts of potassa with vegetable acids 15·3. The fresh plant contains a sulphurous acrid oil, and sometimes nitre.

Conium maculatum. The juice from 100 parts of fresh hemlock yielded green fecula 0·80, albumen 0·31, resin 0·15, gum 3·52, extractive 2·73. (SCHRADER.) This much resembles the cabbage, and takes no account of the poisonous property of hemlock. (See *Conia*, p. 1227.) 100 lbs. of fresh hemlock yield an average produce of 4 lbs. of pharmaceutical extract.

Helvella mitra. Morels contain, according to Schrader, stearin and elain 4·0, sugar 2·0, azotized extractive (*vegetable osmazome*) 29·4, gummy azotized extractive 5·4, albumen 1·2, boletate and phosphate of ammonia and potassa 8·0, fungin 39·6, water 10·4. It is evident that the peculiar flavour and characters of mushrooms, and similar articles of food, are referable to the extractive matter containing nitrogen, and hence resembling an animal product, which I have above termed *vegetable osmazome*: this substance deserves further examination, especially by the culinary chemist.

Hyoscyamus niger. Henbane requires to be minutely examined. (See *Hyoscyamia*, p. 1225.) 100 lbs. of the herb yield, upon an average, 3 lbs. and a quarter of pharmaceutical extract.

Indigofera anil, and *Isatis tinctoria*. (See p. 1119.)

Lichen islandicus. (See *Cetraria*.)

Melissa officinalis. Balm yields, according to Dehne, 1-1920th its weight of volatile oil. The infusion of balm (often drunk as *balm tea*), contains tan, extractive, and gum. Alcohol extracts a little resin.

Pisum sativum. The components of peas are stated at p. 1098.

Rhus toxicodendron. The juice of the leaves of this species, and of the *Rhus radicans* and *vernix*, contains an acrid poison, the nature of which has not been accurately ascertained: it is also a substantive black dye, extremely permanent; cotton or linen imbued with it acquiring a deep black by exposure: the nature of this colouring principle has not been examined, but it seems somewhat analogous to indigo.

5. LEAVES.—*Aconitum napellus*. The leaves of this and other species of monkshood contain a very poisonous principle (alkaloid), which has already been alluded to (p. 1228). Its paralyzing power upon the organs of taste may be perceived by chewing a leaf of the plant; it produces a biting sensation upon the tongue, and taste is impaired for hours afterwards. Bucholz found in the fresh leaves 83·75 per cent. water: the residue, washed with water, left 15 per cent. of woody fibre. On heating the expressed juice, a green and albuminous fecula subsided, amounting, with a little wax, to 5·0. Alcohol abstracts from the inspissated juice of aconite a brown extractive, of a bitter, sourish, saline, and acrid flavour. The part insoluble in alcohol yielded to water 3·75 of gum, and left 1·0 of malate and citrate of lime.

Arbutus uva ursi. The leaves of the whortle-berry are very rich in tannin, and might be much more employed than they are in tanning and

dyeing: they might be abundantly imported from the north of Europe. At present they are only used in medicine as an astringent and tonic, especially affecting the urinary passages.

Atropa belladonna. (See *Atropia*, p. 1224.) 100 lbs. of the fresh herb yield about 2 lbs. 8 oz. of *pharmaceutical extract*.

Cassia senna. The existence of a purgative bitter extractive in these leaves has been above mentioned (*Cathartin*, p. 1238). See also Dr. THOMSON'S *London Dispensatory*. 100 lbs. of senna leaves yield 50 lbs. of *pharmaceutical extract*.

Centaurea benedicta. The dried herb yields volatile oil, chlorophyll and fat oil, brown resin, extractive, bitter principle, sugar, gum, albumen, ligneous matter, and various salts. (MORIN, *Journal de Chim. Med.*, iii. 105.)

Datura stramonium. The fresh leaves of the *thorn-apple* contain 0·64 green fecula, 0·15 albumen, 0·12 resin, 0·60 extractive, 0·58 gum, 0·23 difficultly-soluble salts, 5·15 lignin, 91·25 water. (PROMNITZ.) See *Datura*, p. 1225. 100 lbs. of the fresh herb afford an average produce of 2 lbs. 12 oz. of the *pharmaceutical extract*.

Digitalis purpurea. The leaves of the *foxglove* contain, according to Rein and Haase, a soft, viscid, green resin, soluble in ether, alcohol and volatile oils 5·5, extractive 15·0, superoxalate of potassa 2·0, lignin 52·0, water 5·5 (loss 5). The activity of digitalis resides, according to Haase, in the soft resin. (See *Digitalia*, p. 1229.)

Menyanthes trifoliata. From 100 parts of the fresh leaves, Trommsdorf obtained 15·6 lignin: the green expressed juice deposits, on boiling, 0·49 fecula, from which alcohol and ether abstract 0·12 soft green resin, and 0·37 albumen remains. The filtered juice yields 3·92 of extract, containing gum, inulin, and extractive; the extractive includes a peculiar bitter principle, *menyanthin*, and an azotized substance.

Nicotiana tabacum. (See *Nicotina*, p. 1226.)

Salvia officinalis. 100 parts of fresh *sage-leaves* yield extractive (including an azotized substance and nitrate of potassa) 2·12, gum 1·51, green resin 2·9, albumen 0·43, lignin 15·87, water and loss 77·17. They also yield 0·16 per cent. of a pale-yellow volatile oil; sp. gr. 0·864; soluble in alcohol, but difficultly so in ether. (ILISCH.)

Thea bohea and *viridis*. (See *Thein*, p. 1240.)

6. FLOWERS.—*Anthemis nobilis*. *Chamomile flowers* yield, on distillation, a blue or green essential oil, which becomes yellow when kept. 100 lbs. of the dried flowers yield, upon an average, 2 lbs. 12 oz. of oil, and 3 lbs. 4 oz. of *pharmaceutical extract*.

Arnica montana. These flowers contain an acrid resin, to which their medicinal virtues are ascribed: they also yield a volatile oil, and much tannin, with some gallic acid.

Artemisia santonica. The buds of this plant are used as a vermifuge, under the name of *Semina cinæ*. Their active principle appears to be an acrid volatile oil.

Calendula officinalis. The *marygold petals* contain yellow-green soft resin 3·44, bitter extractive 19·13, gum 1·5, starch 1·25, mucilage (*Calendulin*, p. 1070) 3·50, albumen 0·62, free malic acid with bitter

extractive 6·84, malate of potassa 5·45, malate of lime 1·47, chloride of potassium 0·66, lignin, 62·5. (This gives an excess = 7·33.) The leaves contain the same substances, and a little nitrate of potassa. (GEIGER.)

Caryophyllus aromaticus. Eugenia caryophyllata. Cloves are the calyces and buds of this plant. They contain, volatile oil 18·0, tannin 13, extractive 4·0, tasteless resin 6·0, gum 13, lignin 28, moisture 18. (TROMMSDORF.) By repeated distillation, Ostermeyer obtained 21·5 essential oil; he also obtained the oil of cloves, by *expression*; it then contained a peculiar kind of wax. The average produce of essential oil, as obtained from repeated experiments at Apothecaries' Hall, does not exceed 16 per cent. (See *Oil of cloves*, p. 1143.)

Crocus sativus. From 100 parts of fine *saffron*, Bouillon, Lagrange, and Vogel, obtained yellow volatile oil, with fat, 7·5, wax 0·5, polychroit (p. 1118) 65, gum 6·5, albumen 0·5, lignin 10, water 10. Saffron, as it occurs in trade, is often very damp, and mixed with 5 or 6 per cent. of sand.

Spiræa ulmaria. When the flowers of this plant (*meadow-sweet*) are distilled with their bulk of water, they yield an aromatic water, which on redistillation affords a heavy volatile oil, the properties of which have been described by Pagenstecher of Berne. This oil, according to Löwig (*Ann. de Ch. et Ph.*, Lxi. 219), is a hydracid, composed of 1 atom of hydrogen and 1 atom of a ternary base or radical, represented by ($^{14}car + ^5h + ^4o$). Löwig terms this base *spiroïle*, and the oil *hydrospiroïlic acid*. Chlorine and bromine immediately decompose this acid, producing hydrochloric and hydrobromic acids, and *chloride* and *bromide of spiroïle*. It is also decomposed by potassium, evolving hydrogen and producing a *spiroïlide of potassium*, which, acted on by hydrochloric acid, regenerates the original oil or acid. The hydrospiroïlate of ammonia forms yellow acicular crystals. When gently heated with nitric acid, the hydrospiroïlic acid yields a crystallized product, very soluble in water and alcohol, which Löwig terms *spiroïlic acid*: it forms yellow crystallizable salts with the alkalis: he gives the following summary of these compounds:—

Oil of ulmaria: or hydrospiroïlic acid	=	($^{12}car + ^5h + ^4o$) + h
Chloride of spiroïle	=	($^{14}car + ^5h + ^4o$) + c
Iodide of spiroïle	=	($^{14}car + ^5h + ^4o$) + i
Bromide of spiroïle	=	($^{14}car + ^5h + ^4o$) + b
Spiroïlide of potassium	=	($^{14}car + ^5h + ^4o$) + po
Spiroïlic acid	=	($^{14}car + ^5h + ^4o$) + $4o$
Hydrospiroïlate of ammonia	=	($^{14}car + ^5h + ^4o$) + $h + A$

(See *Salicule*, p. 1232.)

Rosa gallica. Red-rose leaves contain, according to Cartier, a red colouring principle greened by alkalis, gallic acid, tannin, and albumen. From rose leaves which have been infused in water, alcohol abstracts a yellow fixed, and a volatile oil. Dried rose petals, digested in ether, yield oil, gallic acid, tan, and colouring matter. When burned, their ash

contains phosphate of potassa and lime (a vegetable salt of lime), chloride of potassium, silica, and oxide of iron.

Sambucus nigra. Elder flowers have not been minutely examined; they contain a peculiar bitter extractive, and yield, on distillation, a buttery oil, which gives flavour to elder-flower water.

Tilia europæa. The flowers of the lime tree contain, according to Pfaff, a peculiar odorous principle, which passes over in distillation with water, but cannot be separated in the form of volatile oil; but Brossat, from very large quantities of the flowers, obtained a little highly fragrant oil, lighter than water; they also contain tannin, sugar, gum, and lignin. They are well known to attract swarms of bees. When chewed, they appear very mucilaginous. Roux obtained from them, by the action of alcohol, a yellow colouring-matter.

7. FRUITS AND SEEDS.—*Anomum repens.* Cardamom seeds yield 4 per cent. of volatile oil, and 12·5 of resin: the residue consists of mucilage and lignin.

Amygdalis communis. Sweet almonds contain 54 oil, 6 sugar, 3 gum, 24 albumen, (emulsin,) 24 insoluble ligneous matter, 5 skins, 3·5 water, a trace of acetic acid and loss 0·5. (BOULLAY.) Bitter almonds contain the same principles, and the peculiar matters described at p. 1149. The bitter almond-cake which remains, after the expression of the fixed oil, yields an average produce of 9 oz. of volatile oil from the hundred-weight, but much depends upon the mode of distillation.

Artemisia santonica. The seeds contain a substance which has been called *santonin*, or *santonin acid*. (TROMMSDORF, *Ann. der Pharm.*, xi.)

Cannabis sativa. Hempseed contains, according to Bucholz, 19·1 per cent. of oil: the residuary cake contains 24·7 per cent. of albumen, 43·3 of lignin and other insoluble matters; gum, sugar, and a trace of bitter extractive, constitute the residue.

Capsicum annuum. Bucholz found in the pods of *capsicum*, 7·6 wax, 4 acrid resin, 8·6 bitter aromatic extract, 21· gum and extractive, 9·2 gum, 3·2 albumen, 28 lignin, 12 water, loss 6·4. Braconnot terms the acrid soft resin, which appears to constitute the active principle of this pepper, *capsicin*; it fuses when heated, and a single grain, vaporized in an ordinary-sized room, is so diffused through the air as to cause it to excite coughing and sneezing.

Cassia fistula. The pulp of the seed-pods of an American and of an African variety of this tree, yielded, (HENRY,) i., sugar 69·25, gum 2·6, tannin 3·9, moisture 24·25; ii., sugar 61·0, gum 6·75, tannin 13·25, water 19·0. This pulp is medicinally used as a purgative.

Citrus aurantium and *medica.* Neither oranges, nor lemons, have been subjected to any accurate examination. Dried orange-peel yields from 16 to 20 per cent. of an agreeable and apparently peculiar bitter extract. Lemon juice contains, according to Proust, 97·51 water, 1·77 citric acid, with bitter extract, gum, and a trace of malic acid, amounting together to 0·72 per cent.

Coffea arabica. (See *Caffein*, p. 1236.)

Croton tiglium. (See p. 1131.)

Cucumis colocynthis. According to Meissner, the pith freed from

seeds contains fat oil 4.2, a yellow, brittle, very bitter resin, insoluble in ether, 13.2, colocyntin (p. 1236) 14.4, gelatinous matter 3.0, gummy extractive 17.6, lignin 19: the remainder being water and salts.

Cucumis sativus. Cucumbers have been examined by John, who found in the peeled cucumber, green colouring-matter 0.04, sugar, with extractive, 1.66, soluble albumen 0.13, fibres, softened by boiling, and containing traces of phosphate of lime, 0.53, mucilage, free phosphoric acid, salts of ammonia, potassa, lime, and iron, with malic, phosphoric, sulphuric, and hydrochloric acids, 0.5. Water 97.14. The peel of the cucumber contained the same substances, but only 85 per cent. of water, and the fibre resembled fungus.

Cytisus laburnum. (See *Cytisin*, p. 1239, note.)

Delphinium staphisagria. Brandes found in *staves-acre seeds*, stearin 1.4, oil 19.1, gum 3.15, starch 2.40, an azotized extractive, insoluble in alcohol, precipitable by acetate of lead and by infusion of galls, with traces of various salts 30.67, *delphia* 8.10 (see p. 1230), albumen 4.12, sulphates and phosphates of potassa, lime, and magnesia, 5, water 10.

Fragaria vesca. Strawberries have never been analyzed. Dried in *vacuo*, over sulphuric acid, they lose about 90 per cent. According to Scheele, the acid which they contain consists of equal parts of malic and tartaric acids. Their fragranciness passes over in distillation with water.

Humulus lupulus. (See *Lupulin*, p. 1239, note.) Hops yield about 27 per cent. of pharmaceutical extract.

Hyoscyamus niger. Henbane seed contains, according to Brandes, 24.2 oil, 1.4 stearin, a trace of sugar, 1.2 gum, 2.4 mucilage, 1.5 starch, 3.4 extractive, 4.5 albumen, 26. lignin, 24. water: various salts, and a trace of copper? They have since been found to contain hyoscyamia (p. 1225).

Juglans regia. The outer green husk of the unripe walnut contains resinous green matter, tannin, extractive, starch, citric and malic acid, oxalate and phosphate of lime, lignin; and, in the ash, potassa, and oxide of iron. The expressed juice is at first colourless, but becomes brown by exposure: it forms a good dye-stuff.

Juniperus communis. Juniper berries contain a volatile oil and sugar; the former is most abundant in the berries just at their period of ripening; when they are quite ripe and black, it has chiefly passed into resin. The sugar is most plentiful in the deep blue berries, and is partly decomposed when they blacken and dry. Trommsdorf found in the ripe berries, volatile oil (specific gravity 0.853) 1.0, brittle wax, soluble in hot alcohol, ether, and caustic potassa, 4.0, tasteless and inodorous resin 10.0, a peculiar kind of sugar 33.8, gum 7.0, lignin 35.0. The produce of essential oil, from the German berries, as ascertained by repeated distillations at Apothecaries' Hall, amounts upon an average to from 9 to 10 ounces from the 100 lbs., and from the Italian berries to 7 ounces.

Laurus nobilis. Laurel berries have been examined by Bonastre: he found volatile oil 0.8, a crystallizable substance, which he calls *laurin*, 0.5, grease and fat oil 9.9, soft resin 0.8, starch 12.95, gum 8.6, mucilage 3.2, sugar 0.2, lignin 9.4, water 3.2. They also contain a free acid.

Menispermum cocculus. (See *Picrotoxia*, p. 1226.)

Momordica elaterium. (See *Elatin*.) Of the pharmaceutical product, termed *elaterium*, about 1 lb. 8 oz. is obtained from 100 bushels of the gourds.

Myristica moschata. Nutmegs contain, according to Bonastre, fat oil (p. 1134) 31·6, volatile oil 6·0, starch 2·4, gum 1·2, free acid 0·8, lignin 54, (loss 4.) The usual produce in *volatile oil*, in the distillations at Apothecaries' Hall, is 4·5 per cent.

Myrtus pimenta. Allspice has been examined by Bonastre; he analyzed the outer shell and the kernel, with the following results:—

	Husks.	Kernels.
Volatile oil	10·0	5·0
Green soft resin	8·0	2·5
Concrete fixed oil	0·9	3·2
Tannin and extractive	11·4	39·8
Gum	3·0	7·2
Brown gelatinous matter	4·0	3·8
Resinous substance	1·2	1·2
Saccharine extract	3·0	8·0
Malic and gallic acids	0·6	1·6
Lignin	50·0	16·0
Saline ash	2·8	1·9
Moisture	3·5	3·0
Loss	2·2	8·8

Oryza sativa. Carolina rice contains, fixed oil 0·13, sugar 0·29, gum 0·71, starch 85·07, gluten 3·60, lignin 4·8, water 5. Piedmontese rice contains, fixed oil 0·25, sugar 0·05, gum 0·10, starch 83·8, gluten 3·6, lignin 4·8, water 7. (BRACONNOT.)

Piper cubeba. Cubebs yield, on distillation with water, about 10·5 per cent. of volatile oil.

Piper nigrum. The acrimony of black pepper resides in a soft resin or balsam, and in volatile oil. (See also *Piperin*, p. 1234.)

Pisum sativum. Peas. (See p. 1098.)

Prunus cerasus, &c. The analysis of cherries, plums, peaches, and apricots, is given at p. 1051.

Pyrus communis and *malus*. Pears and apples have been examined by Berard, but there are many interesting points respecting them which remain unnoticed, such especially as the rapid change which some of them undergo by the action of oxygen, when they are cut and exposed to air, and during which sugar appears to be formed; he also does not notice pectin or pectic acid, though perhaps it may be formed, as in *apple jelly*, by the action of heat upon their finely-divided lignin; he also overlooks tannin or gallic acid contained in many of those fruits, rendered evident by the blackening of the knives with which they are peeled. The following are the results which he obtained from *Beurré pears*, examined in three states, namely, i. ripe and fresh; ii. kept till mellow; iii. kept till brown or beginning to rot, and having lost 23·15 per cent. of water, &c.

	I.	II.	III.
Resinous green colouring matter	0·08	0·01	0·04
Sugar	6·45	11·52	8·77
Gum	3·17	2·07	2·62
Lignin	3·80	2·19	1·85
Albumen	0·08	0·21	0·23
Malic acid	0·11	0·03	0·61
Lime	0·03	0·04	trace
Water	86·28	83·88	62·72

Apples contain the same ingredients as pears, but in somewhat different proportions, but the cause of *flavour*, and the *aroma* of these fruits, depends upon some volatile principle, probably, which analysis has not detected.

Punica granatum. The rind of the pomegranate is used medicinally as an astringent: it contains, tannin 27·8, resin 0·9, extractive 32·8, gum 34·2, loss 5·1. (REUSS.) No lignin is here mentioned, so that the above are probably the soluble constituents only.

Ribes grossularia. Gooseberries have been analyzed by Berard, with the following results.

	Unripe.	Ripe.
Resinous green colouring matter	0·03	—
Sugar	0·52	6·24
Gum	1·36	0·78
Albumen	1·07	0·86
Malic acid	1·80	2·41
Citric acid	0·12	0·31
Lime	0·24	0·29
Lignin, including the seeds	8·45	8·01
Water	86·41	81·10

Ricinus communis.—This seed, which affords *castor oil* (p. 1131), has been analyzed by Geiger: it yielded 69·09 kernel, and 23·82 husk: this quantity of husk or shell yielded, resin and bitter extract 1·91, gum 1·91, lignin 20·0. The kernel (69·09 parts) afforded, fixed oil 46·19, gum 2·40, albumen 0·5, starch with lignin 20, water 7·09.

Secale cereale. The analysis of *rye* is given above, p. 1098.

Secale cornutum. The *ergot of rye*, which appears to possess such extraordinary influence in promoting the natural contractions of the uterus in child-birth, has been analyzed by Vauquelin and by Pettenkofer, but their researches throw no light upon its medical virtues. It yields a deep brown tincture to dilute alcohol, which on evaporation leaves 18·72 per cent. of wax, which fuses at 212°. The tincture, deprived of wax, affords a transparent brown bitter and sour extractive, which becomes moist in the air; after some days small cubic crystals form in it, which Pettenkofer suspects to be a salt of morphia, but of this there is no evidence. Water takes up a brown bitter extractive from the residue of the ergot insoluble in alcohol. The extraordinary medicinal peculiarities of ergot render an accurate chemical examination of it extremely desirable.

Sinapis alba. The seeds contain, 1. volatile oil; 2. fixed oil; 3. yellow colouring matter; 4. albumen; 5. white crystalline matter; 6. bimalate of lime; 7. citrate of lime; 8. sulphocyanuret of calcium; 9. free sulphur.

Strychnos nux vomica, &c. (See *Strychnia*, p. 1219.)

Tamarindus indica. The pulp of this fruit contains, according to Vauquelin, 12·5 sugar, 4·7 gum, 6·2 jelly, 0·4 malic acid, 9·4 citric acid, 1·5 tartaric acid, 3·2 bitartrate of potassa, 36 ligneous matter, 30 water. Scheele asserts that the whole of the acid in tamarinds is the tartaric acid.

Triticum hibernum. The composition of *wheat* is given at p. 1098.

Vitis vinifera. The juice of sour grapes only contains tartaric acid. The juice of the ripe grape contains odorous matter, sugar (p. 1081), gum, albumen, a trace of malic acid and malate of lime, free tartaric acid, tartrate of lime, and bitartrate of potassa, (also racemic acid?)

Zea mais. According to Gorham, maize, or Indian wheat, contains starch 77, *zein* 3 albumen 2.5, sugar 1.45, extractive 0.80, gum 1.75, sulphate and phosphate of lime 1.5, lignin 3, water 9. According to Bizio, *zein* contains nitrogen as an ultimate element: Gorham regards it as a gluten without nitrogen.

§ XXI. PHENOMENA AND PRODUCTS OF VINOUS FERMENTATION. ALCOHOL.

THE term *fermentation* is employed to signify the spontaneous changes which certain vegetable solutions undergo, placed under certain circumstances, and which terminate either in the production of an intoxicating liquor, or of vinegar; the former termination constituting *vinous*, the latter *acetous*, fermentation.

The principal substance concerned in vinous fermentation is *sugar*; and no vegetable juice can be made to undergo the process, which does not either originally contain it or some other principle, such as starch or starch-gum, capable of being converted into sugar. In the production of *beer*, the sugar is derived from the *malt*; in that of *wine*, from the juice of the *grape*.

The change which *barley* suffers in the operation of *malting* has been already stated (p. 1086), and in a number of other processes starch passes through similar changes, first becoming *gum*, and then *sugar*; and to effect these changes it is only necessary that a portion of sugar should be present, which, when it begins to ferment, leads to the successive conversion of the remaining unchanged starch into sugar. Thus it is, that a small addition of malt to a large proportion of unmalted grain forms a mixture, which, placed under the requisite conditions, tends to vinous fermentation; and that any variety of starch may be rendered applicable to the process, by the addition of any of the ordinary forms of sugar: among common vegetables applicable to this purpose, the *potato* stands pre-eminent, the cause of which will be obvious by reference to its analyses, given in the table at p. 1098.

But a solution of *pure* sugar is not *alone* susceptible of vinous fermentation, and although a mixture of common sugar, and especially of raw sugar and water, will often ferment sluggishly, this arises from what may be termed *impurities* in the sugar.

The substance which, of all others, tends in these cases to induce fermentation, is some form or other of *vegetable gluten* (p. 1091), consequently of an *azotized* or nitrogeniferous substance, for other analogous compounds, and even *animal products*, may be resorted to. But before gluten is fit for this purpose, it must itself have undergone some change, for which the contact of oxygen is apparently required, and of all the forms of modified gluten applicable to the purpose, *yeast*, or, as it is sometimes termed, *ferment*, is the most so.

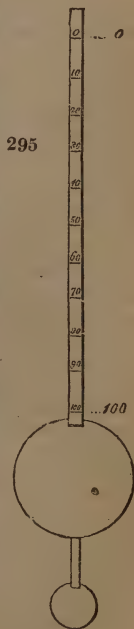
YEAST is the substance which collects, as a scum and sediment, during the vinous fermentation of *wort*, and is derived from the albumino-glutinous parts of the grain: it is generally used in a moist state, but, for convenience, it is sometimes partially dried by pressure and exposure to a

gentle heat; in its moist state it soon runs into putrefactive fermentation at common temperatures, absorbing oxygen, evolving carbonic acid, acquiring a fetid odour, and becoming sour from the formation of acetic acid. Subjected to destructive distillation it yields some ammoniacal products. Perfect desiccation, long exposure to a boiling heat, the action of alcohol, acids, and salts, render yeast ineffective. The nature of the action of the yeast upon the saccharine matter has not been accurately ascertained; but the changes which the latter undergoes during fermentation, have been satisfactorily explained: these we shall recur to, when the nature of *alcohol*, which is the ultimate result, has been examined.

BEER.—In the manufacture of *beer*, the malt is ground and infused in the *mash-tun*, in rather more than its bulk of water, of the temperature of 160° or 180° . At a higher temperature the mixture would *set*, as it is termed; that is, it would become an intractable gelatinous mass, not easily dissolved in, or even diffused through, the mass of water. In the *mash-tun* the malt is *exhausted* by the successive applications of fresh portions of water, and by frequent agitation, which is either effected by paddles or by machinery-power. The nature of this process, and of the manner in which it is performed in our large breweries, can only be adverted to here; they must be visited to form a just conception of the ingenuity of the machinery, and the enormous magnitude of the operations there conducted.

The mixed infusions, as they run from the *mash-tun*, are called *wort*; its principal contents are *saccharine matter*, *starch*, *mucilage*, and a small quantity of *gluten*. The strength of the wort is adjusted by its *specific gravity*, which is usually found by an instrument not quite correctly called a *saccharometer*, since it is influenced by all the contents of the wort, and not by the sugar only. It is a brass instrument, resembling the common hydrometer, of the shape shown in the margin, and so adjusted in weight as to sink to the point marked 0° , in distilled water at the temperature of 70° , and when immersed in a liquor of the same temperature, and of the specific gravity of 1.100, it is buoyed up to the mark 100, just above the bulb. The intermediate space is divided into 100 equal parts, and, consequently, will indicate intermediate degrees of specific gravity. This is the most useful form of the instrument, though not that in common use. Brewers employ complicated and often unmeaning terms to designate the strength of their worts, and speak of the proportion of *saccharine per barrel*, &c. A reform in this department of their business, by the introduction of a new instrument, and of tables showing the quantity of solid matter in worts of given density, and expressed in reference to specific gravity only, would be desirable.

The specific gravity of the wort for ale is usually about 1.090 to 1.100, and for table-beer from 1.020 to 1.030. Those who are curious in the history of *ale* and *porter*, will find the various additions



which are said to be made to those liquors prescribed in various "Treatises on Brewing." *Porter* derives its peculiarities from *high-dried malt*, a certain proportion of which is used in the wort; it is also coloured with *parched malt*, or other colouring materials. As issued from the large breweries, it is a genuine and excellent liquor, but it is generally adulterated and deteriorated by the *publicans*. In Russia, a beverage is made as a substitute for beer, which is called *quaas*: 9 parts of rye-meal, and 1 of undried rye-malt, are made into a paste with water, and left for some days in a warm place, when the mass becomes quite sweet: a wort is then prepared from it, which is run off into casks, where, by the addition of a little yeast, it is brought into slow fermentation: when this terminates it is ready for use. (BERZELIUS.)

The wort is next boiled with *hops*, amounting, upon the average, to one twentieth the weight of the malt, their use being to cover the sweetness of the liquor by their aromatic bitter, and to diminish its tendency to acidify. The liquor is then generally thrown into large, but very shallow, vessels, or *coolers*, or, by other contrivances, is cooled to about 50°, as quickly as possible; it is then suffered to run into the *fermenting vat*, having been previously mixed with a proper quantity of yeast, the use of which has been above stated.

In the fermenting vessel, the different substances held in solution in the liquor begin to act upon each other; an intestine motion ensues, the *temperature* of the liquor increases, and *carbonic acid* escapes in large quantities; at length the evolution of gas ceases, the liquor becomes quiet and clear, and it has now lost much of its sweetness, has diminished in specific gravity, acquired a new flavour, and become *intoxicating* from the presence of *alcohol*.

WASH.—The distillers prepare a liquor, called *wash*, for the express purpose of producing from it ardent spirits*; instead of brewing this from

* The operations of our distilleries would be improved by an alteration in the excise laws: as these at present stand, the duty is charged from calculations, 1. On the quantity and density of the *wash*; 2. On the quantity and density, or strength of the *low wines*, or first products of distillation; 3. Upon the quantity and strength of the *spirit*, or, in other words, of the *alcohol* actually produced: it is presumed, in reference to the *wash*, that the alcohol which it will afford by fermentation will be directly as its *density* (without reference to the *nature* of the matter which it holds in solution). In the *low wines*, and in the *spirits*, the proportion of alcohol is inversely as the density, and the duty is charged in conformity with experiments upon the composition of mixtures of alcohol and water of different densities. I say nothing here of the mode of judging of the value of the wort by its *attenuation* during fermentation, nor of the fallacies to which the different operations are liable, and am

aware of the danger and difficulties of meddling with so important a branch of the revenue; but no scientific person can visit a distillery without at once seeing much that is susceptible of safe and effectual alteration; or peruse the multitudinous documents, and evidence brought before the Commissioners of Revenue Inquiry and before Parliamentary Committees, bearing directly or indirectly upon this subject, without hoping that some remedy may be found for the evils there set forth. In every point of view, two things seem desirable, and apparently not unattainable; the one, that the materials employed as sources of spirit, and the mode of conducting the operations of the distillery, should be, as far as possible, unshackled; the other (a necessary consequence), that the duty should be levied upon the *ultimate produce at the worm-end*, or, in other words, upon the *quantity of absolute alcohol* actually produced, and that the charge should be made in reference to that alone.

pure malt, they chiefly employ raw grain, mixed with a small quantity only of malted grain; the water employed in the mash-tun is of a lower temperature than that requisite in brewing, and the mashing longer continued, by which the starch of the barley is rendered into gum and saccharine matter. The wort is afterwards fermented with yeast.

WINE.—*Wine*, properly so called, is exclusively derived from the juice of the grape. The principal substances held in solution in grape juice are *sugar, gum, gluten, and bitartrate of potassa*. It easily ferments spontaneously at temperatures between 60° and 80° , and the phenomena it gives rise to closely resembles those of the wort with yeast*. After the operation, its specific gravity is much diminished, its flavour changed, and it has acquired intoxicating powers, from the cause before mentioned, namely, the formation of alcohol.

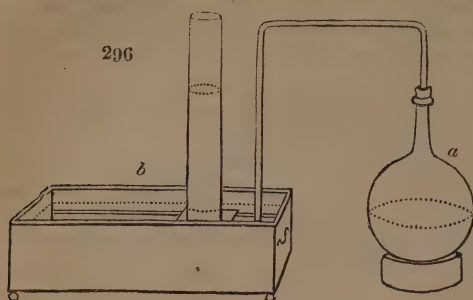
Liquors, under the name of *wine*, are frequently made from *currants, gooseberries*, and other fruits, and when carefully prepared they are not only palatable but excellent. But it is seldom that the requisite attention is paid to their manufacture, (see MACCULLOCH on *Wines*,) and they derive at all times a peculiarity from the presence of malic and citric acids, which are retained in solution; whereas, in grape juice, the acid is chiefly in *tartar*, which is precipitated in proportion as alcohol is formed, and not retained in any quantity, especially in old wines. *Made wines*, as they are termed, are generally strong, in consequence of the quantity of sugar which is used in their production; a considerable proportion of brandy is also often added to them, to prevent secondary fermentation. *Perry* and *cyder* are the fermented juices of *pears* and *apples*, and vary in flavour, strength, and quality, according to the quality of the fruit, and the extent to which the fermentation is carried. *Mead* is a vinous liquor made by dissolving 1 part of honey in 2 and two thirds of boiling water, and adding spices, such as cloves, nutmegs, &c., and a portion of ground malt, and piece of toasted bread dipped in yeast, and suffering the whole to ferment; the Scandinavian mead, according to Berzelius, was flavoured with primrose blossoms.

The changes of the various substances concerned in fermentation can only be fully explained and understood, when the nature of *alcohol* has been examined, but an instructive experiment in reference to this may be made by introducing a mixture of 1 part of sugar, 4 or 5 of water, and a

* A question naturally suggests itself here, why the juice of the grape does not ferment in the fruit itself? We know that ripe grapes, even cut from the vine, exhibit no such tendency; they dry up and shrivel, becoming ultimately *raisins*, but never fermenting, so long as the skin is entire. It was once supposed that this arose from the *gluten* or *ferment* being in distinct vesicles or cells from those containing the *saccharine juice*, and that consequently no fermentation could ensue till the fruit was mashed or broken so as to mix these ingredients. But Gay-Lussac found that when grapes were bruised,

carefully excluded from air, no change ensued; but that even a momentary exposure of the pulp to air or oxygen was enough to communicate to it the power of fermentation. This seems to arise from some recondite action of oxygen on the glutinous principle of the grape, by absorbing which it acquires the properties belonging to *yeast*. It is curious how perfectly the exclusion of *air* is provided for by the natural texture of the grape, which does not allow its ingress, although it admits of the transpiration of *aqueous vapour*, as is shown by the spontaneous desiccation of the berry.

small quantity of yeast, into the bottle *a*, represented in the annexed cut (fig. 296); this mixture gives rise to the same products as *wort* or *grape*



juice: a bent tube issues from the bottle, passing under the inverted jar placed in the water-trough *b*. It will now be found, that all that is requisite to induce fermentation, and the consequent production of alcohol from the above materials, is to subject them to a *due temperature*, say between 70° and 80° ;

they then soon begin to act upon each other, and the principal points to be noticed are, 1. that *carbonic acid* is evolved (without the contact of oxygen or of the external air); 2. that the *sugar* gradually disappears; and, 3. that *alcohol* is gradually formed. Now the inference which we should at once draw from this experiment, and it is not an incorrect one, is, that *sugar*, *minus* carbonic acid, produces alcohol; for, as we shall afterwards find, we have no evidence of the decomposition of water in the process, or of any other source of oxygen than the sugar itself, and it alone can yield the carbon. I have, for the present, put the action of the yeast out of the question, for we shall find it not essential to the theory of the process. The alcohol remains almost entirely in the receiver, in combination with the water, and any other matters that may have accidentally been present; a little, and but a little of it, passes off along with the carbonic acid gas, and this, together with other considerations, renders it advisable, in all cases, to carry on fermentation with as little access of air as possible, and to allow of the escape of the carbonic acid by a comparatively small vent, and even in some cases to pass it into cold water, with a view of collecting, if not the alcohol, the *aroma*, which may sometimes be serviceably applied.

BRANDY, &c.—When wine, or any of the above-mentioned fermented liquors are distilled, they afford a *spirituous liquor*; that from wine is termed *brandy*; from the fermented juice of the sugar cane we obtain *rum*; and from wash, *malt spirit*; and these spirituous liquors, by re-distillation, furnish *spirit of wine*, *ardent spirit*, or *alcohol*.

The different fermented liquors furnish very different proportions of alcohol*, and it has been sometimes supposed that it does not *pre-exist* to

* I regret that in the experiments, the results of which are contained in the table in the text, I did not throughout determine the specific gravity of the wine *before* as well as after distillation, and that the other contents of the wine were not accurately ascertained, for, although these points were made out in some cases, they were not accurately attended to throughout. The following are two of these results:—

1. CAPE WINE.

Sp. gr. <i>before</i> distillation . .	·9824
Ditto <i>after</i> ditto . .	·9742
Alcohol per cent. . . .	23·61

2. SHERRY.

Sp. gr. <i>before</i> distillation . .	·9879
Ditto <i>after</i> ditto . .	·9762
Alcohol per cent. . . .	21·34

See also the tables of the strength of wines in Dr. Henderson's work.

the amount in which it is obtained by distillation (FABBRONI, *Ann. de Ch.*, xxx.); but some experiments which I made upon the subject, in 1811 and 1813, (printed in the *Phil. Trans.* for those years,) tend to show that it is a real *educt*, and not *formed* by the action of heat upon the elements existing in the fermented liquor.

The following Table exhibits the proportion of alcohol, specific gravity ·825 at 60°, by measure, existing in 100 parts of several kinds of wine and other liquors:—

		Proportion of Spirit per cent. by Measure.			Proportion of Spirit per cent. by Measure.
1.	Lissa	26·47	21.	Vidonia	19·25
	Ditto	24·35	22.	Alba Flora	17·26
	Average	25·41	23.	Malaga	17·26
2.	Raisin	26·40	24.	White Hermitage	17·43
	Ditto	25·77	25.	Roussillon	19·06
	Ditto	23·20		Ditto	17·26
	Average	25·12		Average	18·13
3.	Marsala	26·03	26.	Claret	17·11
	Ditto	25·05		Ditto	16·32
	Average	25·09		Ditto	14·08
4.	Port	25·83		Ditto	12·91
	Ditto	24·29		Average	15·16
	Ditto	23·71	27.	Zante	17·05
	Ditto	23·39	28.	Malmsey Madeira	16·40
	Ditto	22·30	29.	Lunel	15·52
	Ditto	21·40	30.	Sheraz	15·52
	Ditto	19·00	31.	Syracuse	15·28
	Average	22·96	32.	Sauterne	14·22
5.	Madeira	24·42	33.	Burgundy	16·60
	Ditto	23·93		Ditto	15·22
	Ditto (Sercial)	21·40		Ditto	14·53
	Ditto	19·24		Ditto	11·95
	Average	22·27		Average	14·57
6.	Currant wine	20·55	34.	Hock	14·37
7.	Sherry	19·81		Ditto	13·00
	Ditto	19·83		Ditto (old in cask)	8·88
	Ditto	18·79		Average	12·08
	Ditto	18·25	35.	Nice	14·63
	Average	19·17	36.	Barsac	13·06
8.	Teneriffe	19·79	37.	Tent	13·30
9.	Colares	19·75	38.	Champagne (still)	13·80
10.	Lachryma Christi	19·70		Ditto (sparkling)	12·80
11.	Constantia, white	19·75		Ditto (red)	12·56
12.	Ditto, red	18·92		Ditto (ditto)	11·30
13.	Lisbon	18·94		Average	12·61
14.	Malaga	18·94	39.	Red Hermitage	12·32
15.	Bucellas	18·49	40.	Vin de grave	13·94
16.	Red Madeira	22·30		Ditto	12·80
	Ditto	18·40		Average	13·37
	Average	20·35	41.	Frontignac (Rivesalte)	12·79
17.	Cape Muschat	18·25	42.	Côte Rôtie	12·32
18.	Cape Madeira	22·94	43.	Gooseberry wine	11·84
	Ditto	20·50	44.	Orange wine—average of six samples made by a London manufacturer	11·26
	Ditto	18·11	45.	Tokay	9·88
	Average	20·51	46.	Elder wine	8·79
19.	Grape wine	18·11	47.	Cider, highest average	9·87
20.	Calcavella	19·20		Ditto, lowest ditto	5·21
	Ditto	18·10			
	Average	18·65			

Proportion of Spirit per cent. by Measure.		Proportion of Spirit per cent. by Measure.	
48. Perry, average of 4 samples	7.26	52. London Porter (average)	4.20
49. Mead	7.32	53. Ditto Small Beer	1.28
50. Ale (Burton)	8.88	54. Brandy	53.39
London (Edinburgh)	6.20	55. Rum	53.68
Ditto (Dorchester)	5.56	56. Gin	57.60
Average	6.87	57. Scotch Whiskey	54.32
51. Brown Stout	6.80	58. Irish ditto	53.90

The wines employed in the experiments upon which the preceding table is founded, were selected with all possible caution as to purity and quality; a given measure of each (saturated, when necessary, with lime or potassa) was carefully distilled nearly to dryness, and the bulk of the distilled product was exactly made equal to that of the original wine by the addition of distilled water. After twenty-four hours its specific gravity was determined, and thence the quantity of alcohol, by reference to GILPIN'S *Tables*. The management of this and similar distillations is well described by Mr. Faraday. (*Chemical Manipulation*.)

The change which wine undergoes in the cask is sometimes connected with a continuance of the fermentation, during which it deposits *tartar* in combination with a peculiar glutiniferous extractive and colouring matter, the terms *red* and *white* tartar being applied to its varieties: the solvent power of the wine over tartar diminishes in proportion to the alcohol which it contains, so that the strongest wines are always in this respect the least acid*. In bottles the same changes continue as in the cask, but they are extremely slow and imperfect; the wine, however, deposits its crust of glutinous extractive and tartar; and it is not uncommon to find in many wines, which have been long in bottle, crystals of tartar, and also of bitartrate of lime, the proportion of all which varies in different wines, and in the same wine according to the time which it had previously been kept in the cask. Another character of wine, which is also much influenced by its age in bottle, is that refined and delicate flavour and odour, termed *bouquet*, or perfume, and upon which so much of the excellence and consequent value of some kinds of wine depends. This quality seems sometimes to depend upon the production of a species of volatile oil, and, in others, upon the formation of something ethereal; but it is so fleeting and destructible, that we have nothing but surmise to offer upon that subject. There is no apparent limit to the time for which some wines may be kept not only in a perfect, but apparently in an improving state, in bottle; such especially are *madeira* and *sherry*. Many of the red wines go on for a time improving, in consequence of the deposition of extractive, tannin, and tartar; they then deteriorate, losing colour and flavour; this is the case with *port*. The aroma or bouquet of *claret* is much improved up to a certain point, and is then apt gradually to decline; yet the deposit from that wine, or the apparent change which it suffers in bottle, is remarkably small: I have seen it after twenty-five years to have deposited nothing more than a thin transparent film of colouring extractive, nearly equal on the

* In cask, too, the wine is changed by evaporation, and the pores of the wood seem to admit of the passage of aqueous vapour, whilst, as is the case with blad-

der, they oppose the transpiration of alcoholic vapour, so that, whilst wine in the wood diminishes in bulk, it probably increases in strength.

whole of the interior of the bottle, together with a slight sediment of the bitartrates of lime and potassa. Some of the rich sweet wines acquire a flavour slightly resembling that of acetic ether after remaining many years in bottle, and during this change they become less and less saccharine.

The *effervescent wines* are bottled before the fermentation, and consequent evolution of carbonic acid, is complete; the consequence is, that that gas continues to be formed, and is necessarily retained by and compressed in the wine. Some of these wines are liable to become *ropy*; the glutinous part of the juice not having been entirely decomposed, in consequence of the incomplete fermentation, separates in the form of a viscid matter, not unlike white of egg. Pure tannic acid, prepared according to Pelouze's method (see p. 1103), is said by Dumas to prevent this effect; or even the addition of powdered galls to the wine before bottling.

The *colour of wines* arises from various causes. *Red wines* derive their colour from the purple husk or skin of the grape, the colouring matter of which becomes soluble in proportion as alcohol is developed, and is reddened by the acid of the juice: tannin is derived from the same source, and perhaps sometimes from the seeds; this gives to red wines their astringency and action on the salts of iron. Some *white wines*, Sauterne and Barsac especially, and I think some of the Rhenish wines, become brown or even blackish, after a few hours exposure to air, which arises either from the presence of some modification of tannin, or from their containing, together with that principle, a trace of some protosalt of iron, which, by the action of the air, becomes peroxidized, and gives the colour. The yellow or brown colour of what are called *white wines* arises from extractive matter; it is also frequently artificial, and the greater part of *brown sherry* is tinted by burned sugar. The colour of *red wines* is also often communicated by various additions, respecting which, and the means of detecting them, some details will be found in BERZELIUS'S *Chemistry* (iii. 949, Wöhler's edition).

ALCOHOL.—This term, which is of Arabic origin, is applied to the intoxicating principle of vinous and spirituous liquors, a fragrant limpid liquid, the properties of which we shall proceed to examine. The history of alcohol is obscure, but its discovery is generally attributed to Raymond Lully, or to Arnold of Villa Nova, or Villeneuve, a chemist who resided at Montpellier, in 1300; but inasmuch as the Egyptians seem to have derived their chemical knowledge from the Oriental nations, and as we know that distillation was practised by them at a very remote period, it is more than probable that alcohol was amongst their numerous discoveries.

The *spirit of wine* of commerce, is alcohol diluted by a variable proportion of water, and generally containing traces of a peculiar *volatile oil*, formed apparently during fermentation, and obstinately retained by the spirit. It is from spirit of wine that we obtain *pure* or *anhydrous*, or, as it is often called, *absolute alcohol*; for this purpose various methods are pursued, among which the following are preferable.

Put some pure lime, which has been well burned, into an alembic or retort, and pour upon it, whilst yet warm, its weight of spirit of wine, leaving the mixture for 24 hours, and then proceeding to distil it slowly

at a temperature below 212° . The first portions which pass over are *pure alcohol*; the last portions, especially if the spirit was not very strong, are apt to contain water, and should therefore be kept apart. The alcohol may be regarded as anhydrous, when its specific gravity is not diminished by a repetition of the distillation. (GAY LUSSAC, *Ann. de Ch.*, lxxxvi. 175; xcv. 311; *Ann. de Ch. et Ph.*, ii. 130.) Acetate, tartrate, or carbonate of potassa are sometimes used to deprive alcohol of water and oil; but they are not so effective as lime*. When carbonate of potassa is used, it should be added warm to the spirit, and the mixture well stirred or shaken; such quantity is requisite as to leave a small portion of the salt undissolved: upon standing at rest, the mixture soon separates into two portions: the uppermost is the alcohol; the lower, an aqueous solution of the carbonate: the alcoholic portion, being carefully decanted from the residue, is to be put into a retort, and about three fourths of it distilled over at a moderate heat into a cooled receiver. Dry chloride of calcium

* The volatile oil of corn spirit is separated in large quantities by Messrs. Bowerbank, under the name of *oil of grain*; it is probably identical with the *volatile oil of potato-spirit*, (the *fusel oel* of the Germans,) which has lately been the subject of a series of experiments by Cahours; it was previously examined by Pelletan and by Dumas. (*Ann. de Ch. et Ph.*, xxx. 221; lvi. 314. LIEBIG, *Chim. Organ.*, 592.) When potato-spirit is distilled, a milky liquid passes over towards the end of the operation which contains the above-mentioned oil mixed with water and alcohol: the rough product contains about half its weight of the latter substances; it boils between 185° and 195° . To purify it it is agitated with water, and after having been left in contact of chloride of calcium, it is redistilled; as soon as the boiling point attains 270° , the recipient should be changed, as it then goes over pure. It is a colourless oily fluid, of a strong odour, agreeable at first, but afterwards eminently nauseous: when its vapour is inhaled, it causes asthmatic pains, coughing, and even vomiting; its taste is very acrid; it is inflammable and burns with a bluish-white flame; it boils at 270° ; its density is 0.8124 at 60° . The density of its vapour is 3.147. It concretes into crystalline plates at -4° ; it produces a stain on paper, which after a time vanishes; it becomes acid in con-

tact of air, is sparingly soluble in water, and mixes in all proportions with alcohol, ether, acetic acid, and oils; it dissolves sulphur, phosphorus, and iodine; it may be mixed without change with solution of caustic potassa and soda, but when heated with solid hydrate of potassa, hydrogen is evolved, and, according to Dumas and Stas, a *valerianate of potassa* is formed. It absorbs much hydrochloric acid with evolution of heat; it gives sulphuric acid a violet tint; distilled with anhydrous phosphoric acid a liquid hydrocarbon is obtained, called by Cahours *amylène*.

According to Cahours, the purified volatile oil above described is the *hydrated oxide* of a basic hydrocarbon, to which he has given the name of *amyle*, but which has not been isolated; its formula is $(10\text{ car} + 11\text{ h})$ and its symbol *ayl*. The anhydrous oxide of amyle is also unknown in a separate form.

Amyle combines with iodine and bromine, forming liquid compounds, which are obtained by mixing iodine and bromine with the hydrated oxide and phosphorus (15 parts of hydrated oxide, 8 of iodine, and 1 of phosphorus). Compounds of sulphuric and of acetic acid with oxide of amyle have also been described, and also several double sulphates. The following are the formulæ and symbols of some of these compounds:—

Amyle	$(10\text{ car} + 11\text{ h}) = \text{ayl}$
Oxide of amyle	$(10\text{ car} + 11\text{ h} + \text{o}) = (\text{ayl} + \text{o})$
Hydrate of oxide of amyle	$(10\text{ car} + 11\text{ h} + \text{o}) + (\text{h} + \text{o}) = (\text{ayl} + \text{o}) + \text{q}$
Bromide of amyle	$(10\text{ car} + 11\text{ h} + \text{b}) = (\text{ayl} + \text{b})$
Bisulphate of oxide of amyle	$(\text{ayl} + \text{o}) + (2\text{ s}) + \text{q}$

may also be used, and is a very effective agent for the separation of the water from alcohol. Caustic potassa is sometimes employed, but it acts chemically upon the alcohol itself. Dried sulphate of lime, sulphate of soda, and some other anhydrous salts eagerly absorptive of water, have also been proposed, but they are inadequate to the total abstraction of the water.

When spirit of wine is put into a bladder, or into a glass vessel with a wide mouth, tied over with bladder, it is found that the aqueous vapour penetrates the animal membrane, in preference to the alcoholic vapour, so that the spirit, by spontaneous evaporation, becomes thus concentrated within the bladder or vessel; spirit of the specific gravity of $\cdot 867$, was thus easily reduced to $\cdot 817$. (*Quarterly Journal*, viii. 381, and xviii. 180.) But this, though a curious experiment, in illustration of the passage of vapours through membranes, is, at all events, only adapted to strengthen common spirit, and not to the preparation of pure alcohol*.

Professor Graham has ingeniously proposed to concentrate alcohol as follows. (*Edinb. Phil. Trans.*, 1828.) A shallow vessel is sprinkled over with coarsely-powdered quicklime, and a smaller one containing spirit of wine is placed just above it; both are covered by a proper bell-glass, upon the plate of an air pump, and the air exhausted till the alcohol begins to boil. Of the vapour which rises, the lime only absorbs the aqueous part, and as water cannot remain under these circumstances in alcohol, unless covered by an atmosphere of its own vapour, it continues in uninterrupted evaporation, whilst the escape of alcohol is prevented by the pressure of its own unabsorbed vapour. If sulphuric acid be substituted as the absorbent instead of quicklime, it absorbs both vapours, and the whole of the spirit evaporates.

Pure alcohol is a limpid, colourless liquid, of an agreeable smell, and a strong pungent flavour. From its action on the system it may be termed *poisonous*; when more or less dilute it is *intoxicating*. The mode in which it kills animals, and the physiology of inebriation have been studied by Orfila and by Sir B. Brodie. (*Phil. Trans.*) It is considerably lighter than water. Its specific gravity varies with its purity; the purest obtained by rectification over lime, or *absolute alcohol*, being $\cdot 791$; as it usually occurs it is $\cdot 820$, at 60° . If rendered as pure as possible by *simple* distillation, it can scarcely be obtained of a lower specific gravity than $\cdot 825$, at 60° . The London Pharmacopœia states *rectified spirit* to have the specific gravity of $\cdot 835$. Alcohol is sufficiently volatile to produce considerable cold during evaporation, though in this respect much inferior to ether: the degree of cold is proportional to the purity of the alcohol. (*Quart. Journ.*, x. 187.)

Alcohol has never been frozen, and consequently is particularly useful in the construction of thermometers intended to measure intense degrees of cold. Alcohol of the specific gravity of $\cdot 7947$, boils at 173° . (Barom. 29.5.) When of a specific gravity of $\cdot 825$, it boils at the temperature of 176° , under the same pressure. When its specific gravity

* Smugglers, who bring spirits into Paris in bladders concealed about their persons, have long known, that although it lost bulk, it acquired strength: hence the preference given to this contraband article.

is as low as $\cdot 800$, its boiling point is $173\cdot 5^{\circ}$; and when raised by the addition of water to a specific gravity of $\cdot 900$, its boiling point, according to Dalton, is elevated to 182° . A table of the boiling points of various mixtures of alcohol and water, founded on M. Groening's experiments, is given in the *Annals of Philosophy*, N.S., v. 313. In the vacuum of an air pump alcohol boils at common temperatures. The specific gravity of the *vapour of alcohol*, compared with atmospheric air, is $1\cdot 613$. (GAY LUSSAC, *Ann. de Ch. et Ph.*, i.) One volume of alcohol produces $488\cdot 3$ volumes of vapour, calculated at the temperature of 212° . According to Berzelius and Dulong, the density of the vapour of anhydrous alcohol is $1\cdot 6004$. (*Ann. de Ch. et Ph.*, xv.) To become vapour, alcohol absorbs only $0\cdot 436$ the heat required to evaporate an equal weight of water. According to Despretz, the latent heat of alcoholic vapour is to that of steam as $331\cdot 9$ to 531 . Dr. Ure (*Phil. Trans.*, 1818) has given a table of the forces of vapour of alcohol at different temperatures. The expansibility of alcohol by heat is such, that 1000 parts (specific gravity $\cdot 817$) at 50° , become 1079 parts at 170° . At 110° , half way between the extremes, the alcohol was at 1039, or half a division below the true mean. The more the alcohol is diluted with water, the greater Mr. Dalton found the disproportion to be between the two parts of the scale. When of the specific gravity $\cdot 967$, corresponding to 75 per cent. of water, the ratio of expansion through the first half between 50° and 170° , was to that through the second half as 35 to 45. (HENRY'S *Elements*, ii. 319; 9th edit.) In the *Ann. de Ch. et Ph.* for January 1837 (Lxiv. 1), there is an elaborate paper by Prof. Muncke of Heidelberg, on the dilatation of absolute alcohol, and of carburet of sulphur, by heat, in which are some valuable facts respecting the maximum of density of those liquids, and their applications to thermometric purposes. It appears that absolute alcohol, of the specific gravity $\cdot 791$, is at its greatest density at a temperature of $- 89\cdot 4^{\circ}$ Centigrade; and it is presumed that it would freeze at $- 92^{\circ}$ of the same scale. The following table of the contraction of alcohol in cooling down from its boiling point, is given by Dumas, as founded upon Gay Lussac's experiments:—

Temp.			Temp.		
Cent.	Fahr.	Volume.	Cent.	Fahr.	Volume.
$78\cdot 14^{\circ}$	173°	1000·0	$38\cdot 4^{\circ}$	101°	954·4
$73\cdot 4$	164	994·4	$33\cdot 4$	92	948·9
$68\cdot 4$	155	988·6	$28\cdot 4$	83	943·6
$63\cdot 4$	146	982·5	$23\cdot 4$	73	938·6
$58\cdot 4$	136	975·7	$18\cdot 4$	65	934·0
$53\cdot 4$	128	970·9	$13\cdot 4$	56	929·3
$48\cdot 4$	119	965·3	$8\cdot 4$	47	924·5
$43\cdot 4$	110	960·0	$3\cdot 4$	39	919·9

Alcohol has a strong affinity for water, and at common temperatures absorbs a little of the aqueous vapour of the atmosphere. It may be mixed in all proportions, with water, and the specific gravity of the mixture is greater than the mean of the two liquids, in consequence of the *diminution of bulk* that occurs on mixture; this may be shown by the following experiment:—

The annexed woodcut represents a tube with two bulbs, communicating with each other, the upper one being supplied with a well-ground glass stopper. Fill the tube and lower bulb with *water*, pour *alcohol* slowly into the upper bulb, and when full put in the stopper. The vessel will now be completely filled, the alcohol lying upon the water; if it be inverted, the alcohol and water will slowly mix, and the condensation that ensues will be indicated by the empty space in the tube. A considerable rise of temperature takes place in this experiment, in consequence of the condensation. Thus, equal measures of alcohol (of a specific gravity of $\cdot 825$) and water, each at 50° , afford, when suddenly mixed, a temperature of 70° ; and equal measures of proof spirit and water, each at 50° , give, under similar circumstances, a mixture of the temperature of 60° .



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When alcohol and water are mixed, the contraction increases till the mixture consists of 100 parts of alcohol and 116.23 of water. According to Rudberg, 100 volumes of this mixture, at 59° , contain 53.739 volumes of anhydrous alcohol, and 49.836 of water; the condensation therefore amounts to 3.575. The specific gravity is 0.927 at 59° . Departing from this point, the contraction produced by fresh additions of water becomes more and more feeble, and terminates in apparent dilatation: thus Tillaye found, that when equal volumes of dilute alcohol, specific gravity 0.954, and water, were mixed, the specific gravity became 0.9768, whereas, if there had been no expansion, the density would have been 0.9772. The following table calculated by Rudberg, from the experimental results of Gay Lussac and Tralles, further illustrates this subject. (*Ann. de Ch. et Ph.*, xlviii. 33.)

Volume of Alcohol per cent.	Contraction, in hundredths of the volume, of the mixture.	Volume of Alcohol per cent.	Contraction, in hundredths of the volume, of the mixture.
100	0	50	3.745
95	1.18	45	3.64
90	1.94	40	3.44
85	2.47	35	3.14
80	2.87	30	2.72
75	3.19	25	2.24
70	3.44	20	1.72
65	3.615	15	1.20
60	3.73	10	0.72
55	3.77	5	0.31

In reference to this table, Dumas remarks, that the maximum of contraction indicates 55 per cent. of alcohol, but that Rudberg's experiments place it at 54 per cent., which is equivalent by weight to 1 atom of alcohol and 3 atoms of water, or 23+27.

The absolute amount of the contraction varies with the temperature; according to Tralles, at 39° it amounts to 3.97; at 52° to 3.77; at 64° to 3.60; and at 100° to 3.31. (See also GILPIN'S *Tables*.)

The *strength* of such spirituous liquors as consist of water and alcohol, is ascertained by their *specific gravity*, and for the purpose of levying

duties upon them, this is determined by the *hydrometer*; but the only correct mode of ascertaining the specific gravity of liquids, is by weighing them in a delicate balance, against an equal volume of pure water, of a similar temperature*.

The facilities, however, in using the *hydrometer* are such as to render it best fitted for the practical purposes of the excise, and, consequently, the Committee of the Royal Society have recommended to the government a form of this instrument, which they consider best adapted to the purpose, accompanied by proper tables; from their *report* I make the following extract, which will explain the most important parts of the inquiry relating to the composition and density of PROOF SPIRIT†.

"With regard to the substance, *alcohol*, upon which the excise duty is to be levied, there appears to be no reason, either philosophical or practical, why it should be considered as *absolute*. A definite mixture of alcohol and water is as invariable in its value as absolute alcohol can be. It is also invariable in its nature; and can be *more readily*, and with equal accuracy, identified by that only quality or condition to which recourse can be had in practice, namely, specific gravity. A *diluted alcohol* is, therefore, that which is recommended by us as the only excisable substance; and as, on the one hand, it will make no difference in the identification, and on the other, will be a great commercial advantage, it is further recommended that the standard be very nearly that of the present proof spirit.

"The proposition of your committee is, that *standard spirit* be that which, consisting of alcohol and water alone, shall have a specific gravity of 0.92 at the temperature of 62° Fahr., water being unity at that same

* There are other methods of judging of the strength of spirituous liquors, which, though useful, are not accurate, such as the taste, the size and appearance of the bubbles when shaken, the sinking or floating of olive oil in it, and the appearances that it exhibits when burned; if it burns away perfectly to dryness, and inflames gunpowder or a piece of cotton immersed in it, it is considered as *alcohol*. The different spirituous liquors leave variable proportions of water, when thus burned in a graduated vessel. But it must be recollected that in rum, brandy, and several other spirits, the specific gravity is often interfered with by extractive, colouring, and saccharine substances, often *fraudulently* added with a view to diminish their apparent strength. In examining these liquors, they should be *distilled* in the manner described above in reference to wine, and the specific gravity of the *distilled portion* will then give an indication of the proportion of alcohol per cent. that may be relied on. In respect, however, to the *excise*, *distillation* is inconvenient, and is, therefore, I believe, only resorted to in extreme or very suspicious cases.

† Hitherto the term *proof spirit* has been but indefinitely employed. Dr. Thomson, quoting the act of parliament of 1762, states, that at the temperature of 60°, the specific gravity of proof spirit should be 0.916; and he also observes that *proof spirit* usually means a mixture of *equal bulks* of alcohol and water; but the specific gravity of such a mixture will, of course, depend upon that of the *standard alcohol*, which is not specified. It appears from GILPIN'S *Tables*, that spirit of the specific gravity .916, at 60°, consists, *by weight*, of 100 parts of alcohol, specific gravity .825, at 60°, and 75 of water; and, *by measure*, of 100 parts of the same alcohol, and 61.87 of water. From the *Tables* of LOWITZ, quoted by Dr. Thomson, from *Cvelli's Annals* (1796; i. 202), equal weights of alcohol, specific gravity .796 at 60° (and which may be regarded as *pure alcohol*), and water, have a specific gravity of .917, which is very near legal proof, and which, according to GILPIN'S *Tables*, contains 62.8 parts per cent. of his alcohol, *by measure*. The *proof spirit* of the *Pharmacopœia (spiritus tenuior)* is directed to be of the specific gravity .930.

temperature; or, in other words, that it shall at 62° weigh $\frac{92}{100}$ ths, or $\frac{23}{25}$ ths of an equal bulk of water at the same temperature. The temperature of 62° Fahr. is recommended as the standard, because it is that at which water was taken in the late national survey and adjustment of weights and measures. The specific gravity of 0.92 is taken rather than 0.918633 (the specific gravity of present proof-spirit at 62°), because the fraction expressing its relation to water is much more simple, and will facilitate the construction of the tables and the verification of the instruments proposed to be used.

"This definition of *standard spirit* appears to your committee to be very simple, and yet as exact as it can be, or as any *other* standard spirit can be. This standard is rather weaker than the old *proof spirit*, in the proportion of nearly 1.1 gallon of the present proof spirit per cent. But this disadvantage your committee consider as trifling compared with the great convenience which will result if the specific gravity of 0.92 be taken rather than 0.918633.

"It may be interesting hereafter to ascertain what proportion of *absolute alcohol* enters into the composition of the recommended standard spirit, should the latter be adopted by the government; but the point possesses not the slightest practical importance in relation to the present question. The proposed standard is in fact more definite, more sure, and more ascertainable than that of the alcohol which it must contain. Philosophers are not yet agreed upon absolute alcohol, and the differences of specific gravity assigned at 60° vary from .7910 to .7980. But assuming the truth to be somewhere within these extremes, the proposed standard would contain nearly one-half by weight of absolute alcohol: .7947 at 59° , BERZELIUS; .7960 at 60° , TURNER from *Saussure*? .7910 at 60° , BRANDE; .7980, CHAUSSIER; .79235 at 64° , GAY LUSSAC.

"In any mixture of alcohol and water the *specific gravity* appears to be the only quality or condition to which recourse can be had for the practical purposes of the excise, in order to indicate the proportion of standard spirit present. Your committee are of opinion that the *hydrometer* is the instrument best fitted in the hands of the excise officer to indicate that specific gravity; and they think it ought to be so graduated as to give the indication of strength, not upon an arbitrary scale, but in terms of specific gravity at a fixed temperature, which, in the present case, should be 62° , or that of the standard spirit. The graduation in terms of specific gravity will not only supply a very minute yet sensible scale for the purpose of ascertaining smaller differences in the density than is done by the present scale, but will also afford an easy means of verifying the instruments when required."

In the *Philosophical Transactions* for 1794, Mr. Gilpin has given a copious and valuable series of tables of the specific gravity of mixtures of alcohol and water, and of the condensation that ensues, with several other particulars. These are extremely useful, as enabling us to ascertain, without difficulty, the relative quantity of alcohol contained in any mixture of known specific gravity. The original tables are very voluminous, and have been variously abridged: but as they are published separately, they should be in the hands of all persons engaged in these inquiries. As far as the experimental chemist is concerned, the following table, by

ALCOHOL is extremely inflammable, and burns with a pale-blue flame, scarcely visible in bright day-light. The heat, however, of its flame is very intense, as may be shown by suspending in it a coil of fine platinum wire, which becomes white-hot. It occasions no fuliginous deposition upon substances held over it, and the products of its combustion are carbonic acid and water, the weight of the water considerably exceeding that of the alcohol consumed. According to Saussure, jun., 100 parts of alcohol afford, when burned, 136 parts of water, the production of which may be shown by substituting the flame of alcohol for that of hydrogen, in the apparatus, fig. 229; and if the tube at its extremity be turned down into a glass jar, it will be found that a current of carbonic acid passes out of it, which may be rendered evident by lime-water.

When alcohol is burned at a lower temperature than that required for its inflammation, as by the action of hot platinum (p. 226), the products of its combustion are very different; the proportion of carbonic acid is less, and acetic acid is formed.

There are some substances which communicate colour to the flame of alcohol; from boracic acid it acquires a green tint; nitre and the soluble salts of baryta cause it to burn yellow, and those of strontia give it a beautiful rose-colour; cupreous salts impart a fine green tinge. The curious monochromatic effect of common salt has been above adverted to (p. 224, *note*).

Mr. Graham has shown that alcohol may, in many instances, be combined with saline bodies, forming, as it were, a substitute for water of crystallization. Such combinations may be called *alcohalates*. They are obtained by dissolving the substances by heat in absolute alcohol, and are deposited as the solution cools, more or less regularly crystallized. They appear to be definite compounds, and in some of them the alcohol is retained by an attraction so powerful, as not to be evolved at a temperature of 400° or 500° . Mr. Graham has examined the alcoholic combinations of chloride of calcium, nitrate of magnesia, nitrate of lime, chloride of zinc, and chloride of manganese. (*Quarterly Journal*, N.S., Dec., 1828.)

The action of chlorine and other halogens on alcohol we shall consider amongst *ethers*. It dissolves nearly all the acids, giving rise to an important and varied class of compounds, resulting from their mutual action: these also will be described in the next section, relating to *ether*; but there are also a series of curious phenomena, arising out of the mere mixture of alcohol and acids, first observed by Chevreul, and subsequently examined by Pelouze. When sulphuric acid, for instance, is mixed with alcohol, the mixture has no action upon any neutral carbonate, and yet it decomposes acetate of potassa, evolving acetic acid. A mixture of alcohol and hydrochloric acid does not act upon carbonate of potassa, but it decomposes the carbonates of soda, lime, strontia, and magnesia. A mixture of alcohol and nitric acid is without action upon carbonate of potassa, but it acts powerfully on carbonate of lime, and of strontia, and slowly on carbonate of soda, baryta, and magnesia. An alcoholic solution of acetic and of tartaric acid decomposes none of the carbonates: a similar solution of citric acid decomposes carbonate of potassa and of magnesia, but not carbonate of baryta, strontia, or lime; and the alcoholic

solution of oxalic acid decomposes carbonate of strontia, of lime, and of magnesia, but not carbonate of potassa. The addition of a small quantity of water does not affect these mixtures, for when a saturated solution of carbonate of potassa is mixed with the alcoholic solution of acetic acid, the carbonate is precipitated without effervescence: an alcoholic solution, therefore, may appear neutral to tests, whilst, in reality, strongly acid. It is difficult to suggest an explanation of these statements.

Alcohol dissolves a small quantity of sulphur, especially at its boiling temperature, but the greater portion is deposited, on cooling, in small brilliant crystals: the solution has a peculiar odour. When a flask of alcohol is suspended in the head of an alembic, containing sulphur, and the latter melted, so that as its vapour rises it may be condensed with that of the alcohol, a reddish-yellow liquid passes over, containing sulphuretted hydrogen: this solution becomes milky upon the addition of water, and appears to contain about a hundredth part of sulphur. A very similar solution may be obtained by passing sulphuretted hydrogen into alcohol, under slight pressure. Alcohol also dissolves phosphorus, taking up about a 240th part at its boiling point, and retaining a 320th part when cold. This solution is luminous in the dark on exposure to air, and produces a beautiful pale, but ineffectual flame, when poured upon hot water. Carbon is insoluble in alcohol, but it dissolves carburet of sulphur, and the solution is decomposed by the alkalis (see p. 574).

Potassium and sodium slowly decompose alcohol at common temperatures; heated with it, they evolve carburetted hydrogen. Potassa and soda are soluble in alcohol, and it is sometimes resorted to as a means of the purification of those alkalis; after a time, however, they begin to act upon each other, and complicated changes ensue; carbonate of the alkali is formed, and carbonaceous matter evolved, on the application of heat; by their slow mutual action, acetic acid, a resin, and a species of brown extractive, appear to be formed. Ammonia and its carbonates are soluble in alcohol: it absorbs a large quantity of ammoniacal, and of several other gases. Lithia, baryta, strontia, and lime, are almost insoluble in alcohol, even in their hydrated states; so also are the fixed alkaline carbonates: their sulphurets are soluble. The greater number of the chlorides*, iodides, and bromides, which are soluble in water, are soluble also in alcohol, and with many of them definite alcoholized compounds are produced: the same is the case with some of the nitrates; but the sulphates are almost all insoluble, hence the use often made in the analysis of mixtures of salts, of the separative power of alcohol.

The uses of alcohol in the arts, and its applications to various economical purposes, are extremely numerous: to the chemist it is a most valuable species of fuel, but we are almost debarred from its use by its high price; and for the same reason many manufactures, in which alcohol is an essential agent, cannot be productively carried on in this country. Its solvent powers, in regard to resins, oils, and other organic products, have been elsewhere noticed: its medicinal and pharmaceutical employ-

* The mutual action of chloride of platinum and alcohol has been studied by Zeise, and his inquiries seem to lead to the existence of a peculiar class of salts, of which hydrocarbon and the chlorides are the elements; he terms them *etherized salts*.

ment is also important; and as an exhilarating stimulant in wines, beer, and other fermented liquors: the mischief, on the other hand, which results from its improper use, is very extensive, as illustrated in the broken constitution of mind and body which characterizes the dram-drinker and the habitual drunkard.

DECOMPOSITION AND COMPONENT PARTS OF ALCOHOL.—When alcohol is passed through a red-hot tube it is decomposed, more or less perfectly according to the temperature, and to the rapidity of its passage: the most accurate experiments upon this subject are those of T. de Saussure (*Ann. de Chim.*, xlii. and lxxxix.); he passed the vapour of alcohol slowly through a red-hot porcelain tube; there was deposited upon its interior a little charcoal, a volatile crystalline substance (probably naphthaline), and a brown empyreumatic oil; and gas was evolved, the specific gravity of which was 0·586, and which was a mixture of carburetted hydrogen, carbonic oxide, and hydrogen.

When alcohol vapour and oxygen are mixed in proper proportions, and fired by an electric spark, a violent explosion ensues, and carbonic acid and water are the results: 1 volume of alcohol vapour requires 3 volumes of oxygen for its perfect combustion, and the result is, 2 volumes of carbonic acid, and 3 volumes of aqueous vapour.

Dumas and Boullay analyzed alcohol by oxide of copper (*Ann. de Ch. et Ph.*, xxxvi. 294), and the results of their experiments, with those of other analysts (corrected for absolute alcohol), give the following as the composition of this fluid:—

				Saussure.	Dumas and Boullay.
Carbon	2	12	52·18	51·98	52·17
Hydrogen	3	3	13·04	13·70	13·31
Oxygen	1	8	34·78	34·32	34·52
Anhydrous alcohol	1	23	100·00	100·00	100·00

It has been above stated, that the specific gravity of alcohol vapour is 1·60, and with this its calculated density, in reference to the above analysis, closely agrees, for

	Vols.	Sp. Gr.
Carbon vapour	1	0·8438
Hydrogen gas	3	0·2064
Oxygen gas	0·5	0·5513
Alcohol vapour	1	1·6015

And these results, expressed in other terms, are equivalent to *olefiant gas* and *water**, or

			Vols.	Sp. Gr.
Olefiant gas	1	14	60·9 = 1	0·981
Water	1	9	39·1 = 1	0·620
Alcohol	1	23	100·0 = 1	1·601

Adopting these views of the atomic composition of alcohol, its *equivalent* is 23, but chemical authorities differ upon this subject, some representing alcohol by the equivalent 46, and considering it as a compound of 1 atom of *etherine* = 28 (see p. 547), and 2 atoms of water = 18, or

* According to Dr. Ritchie, alcohol is resolved by electrochemical decomposition into *olefiant gas* and water.

vitrioli dulce. The term *ether* was applied to it 190 years afterwards by Frobenius, who, in a paper in the *Philosophical Transactions*, described its singular properties; at the end of this paper is a note by Godfrey Hankwitz, Mr. Boyle's operator, mentioning the experiments that had been made upon it by Boyle and by Newton. Since that period the process of etherification has been minutely studied.

PRODUCTION OF ETHER.—1. Ether is usually obtained either by distilling a mixture of sulphuric acid and alcohol, or by suffering alcohol gradually to dribble into the heated and somewhat diluted acid. Mr. R. Phillips' directions for the former process are as follows:—"Mix with 16 ounces of sulphuric acid, an equal weight of rectified spirit, and distil about 10 fluid ounces; add 8 ounces of spirit to the residuum in the retort, and distil about 9 fluid ounces; or continue the operation until the contents of the retort begin to rise, or the product becomes considerably sulphurous; mix the two products, and if the mixture consist of a light and heavy fluid, separate them: add potash to the lighter, as long as it appears to be dissolved; separate the ether from the solution of potash, and distil about nine-tenths of it, to be preserved as *ether sulphuricus*, the specific gravity of which ought to be at most .750." (*Experimenta Examination of the London Pharmacopæia.*)

Preparing ether upon a larger scale, it was found that 14 parts of alcohol (specific gravity .820), mixed with an equal weight of sulphuric acid (specific gravity 1.8), and submitted to distillation, afforded about 8 parts of impure ether (specific gravity .770). 7 parts of alcohol were then added to the residuum, and about $7\frac{3}{4}$ parts more of impure ether drawn off. These products, when mixed, had a specific gravity of about .782, and when rectified by distillation on carbonate of potassa, afforded $10\frac{1}{4}$ parts of ether, of a specific gravity of .735, and about $3\frac{1}{2}$ parts of ethereal spirit, which was employed instead of an equal quantity of alcohol in the next operation.

These processes, when carried on on a small scale, may be conducted in glass retorts with adopters and cooled receivers; but upon the large scale, a leaden still or alembic is most convenient. The ether-apparatus employed at Apothecaries' Hall, consists of a leaden still, heated by means of high-pressure steam carried through it in a contorted leaden pipe; a tube enters the upper part of the still, for the purpose of suffering alcohol gradually to run into the acid in a way which I shall presently explain. The still-head is of pewter, and is connected by about 6 feet of tin pipe, with a very capacious condensing-worm, duly cooled by a current of water; the receivers are of pewter with glass lids, and have a side tube to connect them with the delivering end of the worm-pipe. In conducting this operation, too much caution cannot be observed in avoiding the proximity of fire, and the use of fragile vessels; in all cases in which ether is to be dealt with these cautions cannot be too strictly enforced, as will be more evident when its properties are stated. One of the great advantages in using steam as the source of heat is, that it obviates the necessary vicinity of fire.

2. Boullay's process for the production of ether, which is preferable to the former, is the following:—equal parts of sulphuric acid and of alcohol

(specific gravity .837) are cautiously mixed in a tubulated retort connected with a tubulated receiver by means of a long adapter; the retort is placed in a sand-heat, and the receiver cooled by the proper application of water. An S tube passes air-tight through the tubulature of the retort, the lower end of which is drawn out into a very small or almost capillary opening, and so adjusted as to dip to about two-thirds of the depth of the liquid in the retort; heat is then applied by the sand-bath till the contents of the retort just begin to appear to boil; the fire is then slackened or damped so as to keep up a regular ebullition, and as the apparatus is air-tight, the expansion within is suffered to escape by a siphon tube, which passes through the tubulature of the receiver. When about 2 pints of product have passed over, an equal quantity of alcohol is so gradually suffered to trickle into the retort by the S tube, as not to check ebullition, but to compensate for that which distils over; when, in this way, a quantity of alcohol has been added equal to that contained in the original mixture, the operation is generally left to itself, and as soon as white vapours, and drops of oil appear in the adapter, the fire is withdrawn. The products of this distillation are usually divided into three parts; the first is alcohol with a little ether, which first passes over; the second and largest portion is mixed with a sixteenth of its weight of carbonate of potassa, which abstracts water and sulphurous acid, and decomposes any oil of wine that may chance to be contained in it; this mixture is shaken, and when the ether has acquired a sweet and pure odour, it is rectified by slow distillation from a water-bath till two-thirds of its original bulk have distilled over; this portion is pure ether. The residue of the rectification is mixed with the last portion of the original distillation, and kept for some days in contact with the carbonate of potassa before used, and a little water and peroxide of manganese are added so as to get rid of the sulphurous acid; when this is done, the stratum of ether is drawn off and rectified, but it never equals in quality that of the former part of the process.

It will be observed that, in this process, a large additional quantity of alcohol is gradually added, and converted into ether by the original portion of sulphuric acid: and by obvious contrivances, the same thing may be effected with the still and apparatus used on the large scale.

3. Mitscherlich (in the first volume of his *Lehrbuch der Chemie*) has added some important facts to the preceding details, and has given a form of apparatus for the production of ether which well illustrates it. It consists of a large flask or bolthead, the mouth of which is closed with a cork having three perforations, one of which allows the insertion of a thermometer by which the temperature of the contents of the flask can be regulated; the second admits of the passage of a small tube terminating at its upper end in a funnel, and at its lower, within the flask, in a capillary opening which dips into the liquid; from the third aperture a tube issues for the conveyance of the vapours generated within the flask into a proper condenser immersed in cold water; the end of this tube within the flask is slanted off, so that liquid forming in it may drop back into the flask and not obstruct the free egress of the vapour. Absolute alcohol is first poured into the flask, and then sulphuric acid, somewhat diluted, is gradually added, care being taken to prevent the heating of

the mixture above 250° (120° Cent.). The proportions are 100 parts of sulphuric acid (which already contains 18.5 of water) diluted with 20 parts of water, and mixed with anhydrous alcohol, in the proportion of 50 parts to every 100 of concentrated acid. To this mixture heat is applied, and it is kept boiling till the thermometer within the flask indicates 284° (140° Cent.); two strips of paper are then pasted upon opposite sides of the flask to indicate exactly the bulk of its contents, by showing the level of the liquid within it; alcohol is then suffered to flow in by the funnel-tube, the supply being so regulated as to maintain the boiling point at 284° . If, having set out with 9 ounces of sulphuric acid, $1\frac{1}{2}$ oz. of water, and 3 ounces of alcohol in the flask, the specific gravity of each successive 2 ounces that pass over into the receiver attached to the condenser be determined, that of the first 2 ounces will be 0.780, that of the two following 0.788, and this gradually increases to 0.798, at which the density generally arrives by the ninth or tenth ounce, and then remains constant; that being nearly the density of the alcohol used.

If the precaution just stated respecting the adjustment of the temperature be strictly attended to, any quantity of alcohol may be etherized by the same portion of acid, which is no further altered than by foreign matters which may be accidentally present, or by the volatilization of a minute portion along with the ethereal vapour.

The liquid which passes over through the condensing apparatus into the receiver, separates into two parts, the lighter stratum being ether, with a little alcohol and water; and the heavier, water, with a little alcohol and ether; and when the process has been carefully conducted, the weight of these products exactly corresponds with that of the alcohol consumed. In an experiment in which a large quantity of product had been obtained, it was found to consist of 65 ether, 18 alcohol, 17 water; now the quantity of water which should have been evolved in the production of 65 parts of ether is 15.4; so that the practical is as near to the theoretical result as could be expected, considering the impossibility of preventing the loss of ether by evaporation, and including errors of experiment. Careful manufacturers obtain from 100 parts of spirit of wine, containing 76 parts by weight of anhydrous alcohol, 60 parts of ether of the specific gravity 0.727; according to calculation, they should obtain 58 parts of ether of 0.724. With this diluted alcohol, the water which passes over is of course in greater quantity than when absolute alcohol is used.

The ether of commerce almost always contains alcohol, which materially affects its density; sometimes it also contains water, which is the case with what is termed *washed ether*; and if ether has been long prepared, it is often slightly acid, and leaves a peculiar odour when rubbed upon the hand. In order to procure from it perfectly *pure ether*, it must be well shaken in a close vessel with about twice its bulk of water, and allowed to separate upon its surface; it is then poured off, and a sufficient quantity of well-burned lime added to it, by which the water which it had acquired by the agitation is abstracted; the mixture of ether and lime is then distilled, care being taken to prevent all escape of vapour, and to keep the condensing-receivers cold, and the first third that distils over may be considered as *pure ether*, free from alcohol and from water.

PROPERTIES OF ETHER.—Ether is a transparent, colourless, limpid liquid, of a peculiar penetrating and agreeable odour, and a pungent and sweetish taste; it is highly exhilarating, and produces a remarkable species of intoxication when its vapour is respired mixed with air. It is neither acid nor alkaline; it has a high refractive power in regard to light, and is a non-conductor of electricity.

The specific gravity of ether, at 68° , is according to Saussure 0.715; according to Gay Lussac its specific gravity (in reference to water at its maximum density) at 90° is 0.69739; at 76° = 0.71192; at 68° = 0.7154; and at 54° = 0.7237. Assuming the water at the same temperature as the ether, its specific gravity at 68° is = 0.71654; and at 58° it is = 0.7240. According to Dumas and Boullay the specific gravity of ether at 68° is = 0.713. This exactly agrees with my own determination of the specific gravity of ether at 60° which had been washed and distilled off quick-lime; this refers to water at 40° .

Ether is eminently volatile*. At mean pressure, it boils according to Gay Lussac at 96.5° . Ether of the specific gravity of .720 may be said to boil under a pressure of 30 inches, at 98° . Upon this subject, however, the best authorities vary a little, in consequence, perhaps, of variations in the density of the ether and of barometrical pressure, circumstances which easily influence the boiling point of this liquid; it is also much affected by the nature and cleanliness of the vessel in which the experiment is made. Dr. Bostock found that, in a clean glass tube, it might be heated considerably above its boiling-point, but that when in that state a few metal filings or other solid particles were thrown into it, its temperature instantly fell, and it entered into ebullition. (*Ann. of Phil.*, 2nd series, viii. 296.) The extreme volatility of ether renders it impossible to pour it from one vessel to another without losing a portion by evaporation, and its vapour, in consequence of its density, is easily discerned passing off from the liquid: it is this which renders it so dangerous to expose ether near to, and especially above, the flame of a candle. This density of ethereal vapour is well shown by dipping a flock of cotton into ether, and placing it within a glass tube of about an inch diameter, and 18 or 20 inches long; the ethereal vapour will descend and escape from the lower end of the tube, where it may be inflamed by a lighted taper, but none rises to the upper end of the tube. If the lower end of the tube be drawn into a point and bent upwards, the ethereal vapour may there be burned in the manner of a gas-light.

The great density of ethereal vapour was first noticed by Dr. Ingenhouz. (*Nouvelles Expériences*, p. 180.) Experiments have been made upon this subject by Dalton (*Manchester Mem.*, 2nd series, iii. 260) and by Gay Lussac and Despretz. (*Ann. de Ch. et Ph.*, i. 218, and xxi. 143.) The results of the latter experimentalists closely agree, and place the density of ethereal vapour, at mean pressure and temperature, between 2.5808 and 2.5860 in reference to air as = 1. At the temperature of 212° 1 volume of ether gives 212 volumes of vapour.

* See the experiments at pp. 175 and 183, (figs. 63 and 67,) in reference to the low boiling point, and the cold produced by the evaporation of ether. It is obvi-

ous that were it not for atmospheric pressure we should only know ether as a gas or vapour, for in vacuo it boils at all temperatures.

The elastic force of ethereal vapour is shown by letting a drop or two pass up into the vacuum of a barometer, when it instantly depresses the mercury several inches, more or less according to the temperature: hence also, when thrown up into gases standing over mercury, it greatly augments their bulk. The following table shows the result of Mr. Dalton's experiments on the force of ethereal vapour at different temperatures.

Temp.	Force of Ethereal vapour.	Temp.	Force of Ethereal vapour.
36°	7.5 inches.	173°	120.0
64	15.0	212	208.0
96	30.0	220	240.0
132	60.0		

The volume of liquid ether is extremely affected by change of temperature; much more so than that of alcohol. The following are the results of Gay Lussac's experiments upon this subject, in which the volume of ether, at its boiling point, is assumed = 1.000.

Cent.	Fahr.	Bulk.	Cent.	Fahr.	Bulk.
35.66° . . .	95° . . .	1000.0	5.66° . . .	42° . . .	953.6
30.66 . . .	87 . . .	991.9	0.66 . . .	33 . . .	948.0
25.66 . . .	76 . . .	983.8	- 4.33 . . .	26 . . .	941.3
20.66 . . .	69 . . .	975.8	- 9.33 . . .	14 . . .	934.5
15.66 . . .	60 . . .	968.2	-14.33 . . .	4 . . .	928.0
10.66 . . .	51 . . .	960.9	-19.33 . . .	3 . . .	922.0

According to Fourcroy and Vauquelin, ether congeals or crystallizes when cooled down to -46° (*Ann. de Ch.*, xxix. 289), but neither Thenard nor Bussy have been able to freeze it, so that the ether used by the former experimentalists was probably impure*.

When ether is inflamed it burns away with a bright and slightly sooty flame, leaving no residue, and producing carbonic acid and water†. By

* From the experiments of Gerard it appears that ether passes more readily through a capillary orifice than water, and water than alcohol; the relative times for equal measures of each fluid, at the temperature of 54° , being 101" for ether, 349" for water, and 856" for alcohol. The comparative heights to which these three fluids rose in the same capillary tube were = 6 for ether, 9 for alcohol, and 13 for water. (*Ann. de Ch. et Ph.*, vi. 239.)

† When ether is passed over red-hot platinum wire, or consumed in the lamp without flame, an acid is produced, which was first examined by Mr. Daniell. (*Quar. Jour. of Science and Arts*, vi. 318.) He obtained it by placing the lamp, filled with ether, and properly trimmed with a coil of glowing platinum wire, under the head of an alembic, in which the vapour was condensed, and collected in a phial applied to its beak. Lampic acid, for so he termed this product, is colourless, sour, and pungent; its vapour is very irritating, and its specific gravity, when purified, about 1.015. It reddens vege-

table blues, and decomposes the alkaline carbonates with effervescence. When added to the solutions of silver, gold, platinum, mercury, and copper, and the mixture heated, the metals are thrown down in the metallic state. On distilling lampate of mercury, made by digesting peroxide of mercury in the acid, the lampic acid passes over in the form of a very dense liquid with an intensely suffocating odour. These properties first induced Mr. Daniell to consider this product as a peculiar acid, but, upon further inquiry into its nature and combinations (*Quar. Jour.*, xii. 64), he found the acid to be the acetic, combined with a compound of carbon and hydrogen, differing from alcohol and from ether, and conferring upon it those properties, in respect to certain metallic solutions, which have been just mentioned. The more recent researches of Döbereiner and Liebig have shown that this acid is identical with the compound which they have termed aldehydic or acetulous acid, and which will be subsequently described (p. 1331).

passing ether into a jar supplied with a jet and stop-cock, standing over warm water, its vapour may be burned at the jet: if its vapour be mixed with about 10 volumes of oxygen it explodes by an electric spark, but with smaller quantities of oxygen, or with air, this combustion is only imperfect.

Exposed to air and light, as in bottles which are frequently opened, ether becomes less perfectly volatile, and less capable of dissolving fixed oil, in consequence of the formation of a little acetic acid. The presence of this acid is not at first apparent because it forms acetic ether, but it gives the ether a peculiar odour, and in time it becomes acid to tests. (PLANCHE, *Ann. de Ch. et Ph.*, ii. 273.) The best way of preserving ether is to keep it in small well-stopped bottles, or even in sealed tubes, and in a dark place. Gay Lussac, in some very old ether, which had been occasionally exposed to air, and the boiling point of which was elevated to 130° , found an oily matter, crystallizable, and of an ethereal odour. According to Döbereiner, ether which has been exposed to air, contains free nitrogen, the oxygen having combined with the ether.

Ether is soluble to a certain extent, in water, of which 9 parts take up 1 of ether; and washed ether retains about a tenth part of water.

When a little ether is introduced into chlorine, the gas is absorbed and peculiar compounds result, which we shall afterwards examine; when bubbles of chlorine are passed into ether, they often cause inflammation, and when a small quantity of ether is poured into a large jar of gaseous chlorine, previously warmed, it occasionally happens that a considerable explosion ensues. If the ether be cooled, and chlorine passed into it, hydrochloric acid is formed, together with a fluid compound containing chlorine, which, when saturated with potassa, produces chloride of potassium and acetate of potassa.

Iodine and bromine are soluble in ether, and gradually react upon and decompose it. The action of bromine upon ether has been studied by Löwig. (*Ann. de Ch. et Ph.*, Lxi. 279.) When ether is saturated with bromine, and the mixture left for ten or twelve days, it is entirely decomposed; the products are 1 formic acid? 2 hydrobromic acid, 3 hydrobromic ether, 4 heavy bromic ether, 5 bromal; the four first products may be separated by distillation, and the *bromal* remains; it may be purified by mixture with water, and in the course of twenty-four hours crystals of *hydrated bromal* are formed. Bromal is composed of

				Löwig.
Carbon	4	24	8.71	8.64
Hydrogen	1	1	0.36	0.38
Oxygen	2	16	5.80	6.33
Bromine	3	234	85.13	84.65
Bromal	1	275	100.00	100.00

Hydrate of bromal consists of

Bromal	1	275	88.5
Water	4	36	11.5
Crystallized hydrate of bromal	1	311	100.0

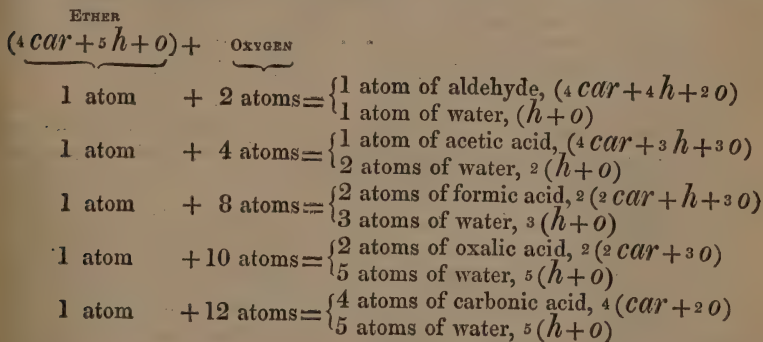
When hydrate of bromal is boiled with an alkaline solution, 2 atoms

are resolved into 2 atoms of formic acid, 2 of bromoform, and 6 of water.

Ether dissolves a small quantity of sulphur (1-80th), which is not thrown down by the addition of a little water; the solution smells of sulphuretted hydrogen, and by slow evaporation deposits acicular crystals of sulphur. I once had occasion to saturate about a pint of ether with sulphuretted hydrogen gas: the solution was put aside in a well-stopped bottle for some months, and had then deposited small octoëdral crystals of sulphur. Ether dissolves more than 2 per cent. of phosphorus (1-37th); the solution, when concentrated by evaporation, deposits crystals of phosphorus; it is luminous in the dark when in contact of air; and, poured upon hot water, produces a brilliant column of luminous vapour. Exposed to air this solution becomes sour; it deposits phosphorus when mixed with water or with alcohol. It gradually deposits a red matter, especially when exposed to light.

A small quantity of sulphuric acid added to ether produces no effect, but a mixture of equal parts of ether and the acid blackens, and yields, on distillation, oil of wine, olefiant gas, acetic and sulphurous acid, and water; it leaves a resinous matter and charcoal. Anhydrous sulphuric acid decomposes ether, and produces, according to Liebig, "isæthionic and althionic acids, oil of wine, and sulphate and bisulphate of oxide of ether; if heat be used, these products are decomposed, and sulphate of oxide of ethule, oil of wine, water, and ether, together with acetic, formic, and sulphurous acids, carbonic oxide, and olefiant gas distill over."

Heated with nitric acid ether yields carbonic, acetic, formic, and oxalic acids, and aldehyde. The following, according to Liebig, are the results of this action of nitric acid on ether.



Ether absorbs a large quantity of hydrochloric acid, and chloride of ethule is obtained on distilling the concentrated solution.¹

Ammoniacal gas is abundantly absorbed by ether. Potassa and soda act feebly upon it, and give rise, among other products, to acetic and formic acids which unite to the alkali. Potassium and sodium are slowly converted into potassa and soda when kept in ether, and hydrogen is disengaged; but the mutual action of these substances has not been accurately studied. The easily oxidizable metals, when kept in ether, such as lead, zinc, iron, and tin, are, according to Berzelius, slowly oxidized and form acetates. Many of the salts are also soluble in ether, such as

chlorides of gold, platinum, iron, and uranium; the property which ether has of abstracting these salts from their aqueous solutions has been adverted to under the history of the respective metals. The fixed and volatile oils, many of the resins, caoutchouc, various forms of extractive, the alkaloids, and some other vegetable principles, are more or less soluble in ether; hence ether is often employed in the proximate analysis of organic products, as a means of separating them from each other.

Alcohol and ether mix in all proportions, and, as above stated, the ether of commerce generally contains alcohol, which affects its density and its boiling point: the means of abstracting the alcohol have been before mentioned. *Hoffman's anodyne liquor*, and the *spirit of ether* of Pharmacy, are such alcoholic solutions.

The following table of the density of various mixtures of ether (specific gravity 0·720) with alcohol (specific gravity 0·830), is constructed from direct experiments by Mr. Dalton.

Ether.	Alcohol.	Sp. Gr.	Ether.	Alcohol.	Sp. Gr.
100	+ 0	0.720	40	+ 60	0.792
90	+ 10	0.732	30	+ 70	0.804
80	+ 20	0.744	20	+ 80	0.816
70	+ 30	0.756	10	+ 90	0.828
60	+ 40	0.768	0	+ 100	0.830
50	+ 50	0.780			

COMPOSITION OF ETHER.—When the vapour of ether is passed through a red hot tube, it is decomposed, and resolved into aldehyde and carburetted hydrogen gases (olefiant and fire-damp?)*.

Analyzed by passing it through red hot oxide of copper, ether furnishes the following elementary composition:—

				Dumas and Boullay.
Carbon	4	24	64·87	65·0
Hydrogen	5	5	13·51	13·8
Oxygen	1	8	21·62	21·2
Ether	1	37	100·00	100·0

The specific gravity of *ether vapour* has been shown to be 2·586, and with this, in reference to the above analysis, its calculated density is perfectly consistent, and is as follows:—

	Vols.	Sp. Gr.
Carbon-vapour	2	1·687
Hydrogen gas	5	0·344
Oxygen gas	0·5	0·551
Ether-vapour	1	2·582

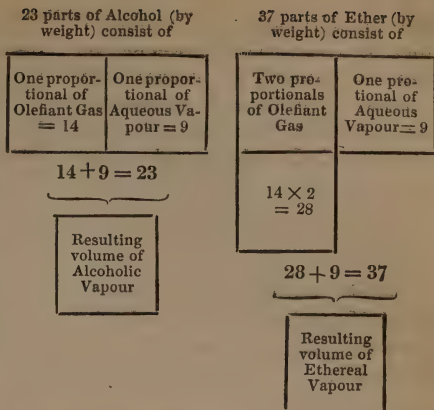
These results may be stated, in other terms, as follows:—

			Vols.	Sp. Gr.
Olefiant gas	2	28	75·7 = 2	1·962
Water	1	9	24·3 = 1	0·620
Ether	1	37	100·0 = 1	2·582

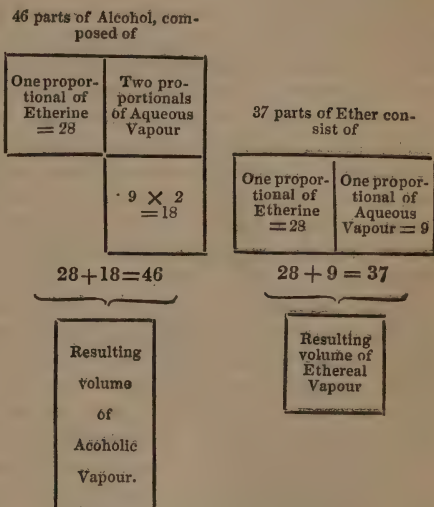
* According to Liebig 2 atoms of ether are resolved into

1	atom of aldehyde	4 car + 4 h + 2 o
2	„ light carbo-hydrogen	2 car + 4 h
1	„ olefiant gas	2 car + 2 h
2	„ ether	8 car + 10 h + 2 o

We thus, therefore, may consider 37 as the *equivalent* of ether; and if we substitute 1 atom of quadrihydrocarbon or *etherine*, for 2 of olefiant gas, ether will then be a *hydrate of etherine*, and the conversion of *alcohol* into *ether* will consist in abstracting from it 1 atom of water: these views are represented in the annexed diagrams, in which both *weights* and *volumes* are evident.



Or, assuming that view of the composition of alcohol and of ether which represents the former as a *binhydrate*, and the latter as a *hydrate of etherine*, we have

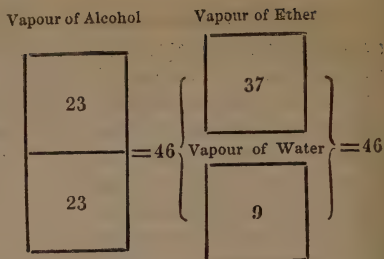


In either view of this subject it is obvious that alcohol is convertible into ether, by the removal of one-half of its elementary oxygen and hydrogen, which are in the proportions that form water.

We have therefore the following as the formula of ether: ($4\text{ car} + 5\text{ h} + \text{o}$), or, $2(2\text{ car} + 2\text{ h}) + \text{q}$, or, $(4\text{ car} + 4\text{ h}) + \text{q}$.

Berzelius has adopted another view of these subjects, to which I have elsewhere adverted, and which consists in regarding ether as the oxide of a *compound inflammable basis*, which he terms *ethyle* or *ethule*, (from *ether* and $\upsilon\lambda\eta$, *principle*;) and which, from reference to the preceding results, will obviously consist of 4 atoms of carbon, and 5 of hydrogen, and be represented therefore by the equivalent 29, (or, $6 \times 4 = 24 + 5$;) and *ether* will contain 29 ethule + 8 oxygen = 37. According to this view alcohol is a *hydrate of ether*, consisting of 37 ether + 9 water = 46; hence the necessity of the double equivalent for alcohol, to which I have alluded;

And in reference to this view 1 atom of alcohol, (or 2 volumes of alcoholic vapour,) is resolved into 1 atom of ether and 1 atom of water, (or into 1 volume of ether vapour and 1 volume of water vapour.)



Ethule, according to Liebig, has not been isolated: in the *Philosophical Magazine* for 1839 (vol. xix., p. 543), a mode of obtaining it in a separate state is noticed by Löwig, but the process is not very intelligible.

THEORY OF ETHERIFICATION.—In the preceding statement respecting the formation of ether, I have purposely avoided adverting to certain intermediate changes which the alcohol undergoes, and which we shall presently proceed to examine, in order to direct attention to the principal and most obvious, or final result, which is, its resolution into ether and water, whilst, at the conclusion of the process, the sulphuric acid remains unchanged. It will be evident, from the details which have been given, that 2 equivalents of alcohol are converted into 1 of ether and 1 of water; or that 1 volume of the vapour of ether, and 1 volume of aqueous vapour, are the results of this decomposition of 2 volumes of alcoholic vapour.

This important fact, namely, that alcohol is converted into ether by the abstraction of water, or its elements, was first demonstrated by Gay Lussac, who conceived that the influence of the sulphuric acid consisted in this abstraction of water; and the well-known attraction of that acid for water seemed to sanction the conclusion, which was further strengthened by the fact, that a similar ether might be formed by the agency of arsenic, phosphoric, and fluoboric acids, all of which, like the sulphuric, are strongly attractive of water. But in this explanation the following circumstances were overlooked, namely, first, that water may be abstracted from alcohol by the alkalis, or by chloride of calcium, or by passing it through a red-hot tube, and yet nothing like ether is the result; secondly, that water passes over during the whole of the process along with the ether, with which the acid ought to combine, in preference to decomposing or dehydrating the alcohol; thirdly, that ether is not produced by the action of anhydrous sulphuric acid on alcohol; and, fourthly, that ether is never produced except by the aid of heat.

Mitscherlich considers the formation of ether as a case of *decomposition by contact*, conceiving that, at a certain temperature, (regulated by the dilution of the acid,) alcohol, on merely coming into the contact of sulphuric acid, is resolved into ether and water: he cites the decomposition of oxygenated water, or peroxide of hydrogen, by gold, silver, and peroxide of manganese, and the action of spongy platinum in determining the combination of certain gases, together with the conversion of sugar into alcohol and carbonic acid by the *contact* of ferment,

as parallel cases; but if these were parallel cases they still throw no light upon that before us, and the explanation merely substitutes one difficulty for another.

That the mere *abstraction of water* from the alcohol by the sulphuric acid, either in consequence of its affinity, or by contact, is not the sole or efficient cause of the formation of ether, was shown, first by Dabit (*Ann. de Ch.*, xxxiv. 289), afterwards by Sertuerner and Vogel, and subsequently by Hennell. (*Phil. Trans.*, 1826 and 1828.) Sertuerner found that the sulphuric acid underwent more complicated changes; and he called the new acid, which he conceived to result from these changes, *Ænothionic acid*. Vogel afterwards found, that by the action of the alcohol, the sulphuric acid lost much of its power of precipitating the soluble salts of lead; and he called the acid into which it was converted, *Sulphovinic acid*, which term we still retain. Mr. Hennell's experiments prove, that the mutual action of the sulphuric acid and alcohol is *immediate* upon mixture; that its saturating power is diminished; that the new acid forms soluble salts with baryta, and oxide of lead, and other distinct combinations*; he then goes on to show that this acid, the *sulphovinic*, contains sulphuric acid and quadrihydrocarbon, or etherine; and considers it as the agent by which etherine is first formed, and then so evolved, as to unite with water to form ether: in short, that in the conversion of alcohol into ether, the formation of *sulphovinic acid* is an intermediate and a necessary step, and that this acid when anhydrous is a *bisulphate of etherine* ($4\text{ car} + 4\text{ h} + 2\text{ s}$).

Liebig admits that the formation of *sulphovinic acid* is an essential step in the process of etherification, but he takes a different view of the nature of that acid, and considers it as a compound of 2 atoms of anhydrous sulphuric acid, 2 of water, and 1 of etherine; or, assuming alcohol to be a *binhydrate of etherine*, and its equivalent 46, he regards *sulphovinic acid* as a *bisulphate of alcohol*†. Adopting this theory, we assume that the *formation of sulphovinic acid* is the consequence of the mutual action of the alcohol and sulphuric acid upon each other, at a *given temperature*,

* The *immediate change* in the sulphuric acid is rendered evident by the following experiments: 440 grains of sulphuric acid were mixed with an equal weight of alcohol, specific gravity .820; the mixture, when cold, was diluted with water, and saturated by carbonate of soda, of which it required only 398 grains; whereas 440 grains of sulphuric acid saturated 555 grains of the same carbonate: here, therefore, two-sevenths of the acid seem to have been saturated by, or to have entered into some new combination with, the alcohol.

440 grains of sulphuric acid were mixed, as before, with its weight of alcohol, and the mixture poured into a solution of acetate of lead; 542 grains of sulphate of lead only were precipitated; whereas the same quantity of sulphuric acid not acted upon by alcohol, threw

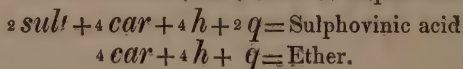
down 1313 grains of sulphate of lead, so that four-sevenths of the acid had lost its power of precipitating oxide of lead.

Vogel and Gay Lussac have attributed this loss of saturating power to the formation of hyposulphuric acid; and they regard the hyposulphates and sulphovicates as only differing in the latter containing ethereal oil, which in some way acts the part of water of crystallization. But that this is not a correct view of the phenomena will appear from the following experiments on the nature of oil of wine, and of *sulphovinic acid*.

† We have seen above that *hydrocarbon*, under certain circumstances, performs the part of a *base* (p. 553). Liebig's view, therefore, of *sulphovinic acid*, represents it as a *hydrated bisulphate of etherine*.

which temperature is ensured by the state of dilution of the mixture of sulphuric acid, alcohol, and water: if the acid be too dilute, the temperature at which the mixture boils is not high enough to form the sulphovinic acid, and alcohol passes over unchanged; if it be too concentrated, the temperature is too high, and the alcohol is decomposed, and olefiant gas is formed; it is between these extremes that the formation of sulphovinic acid ensues; and the mixture most favourable to it, as appears from Mitscherlich's statement (p. 1277), consists of 100 parts of common sulphuric acid, 20 of water, and 50 of anhydrous alcohol.

Now, these proportions are very nearly equivalent to 1 atom of common or hydrated sulphuric acid, 1 of water, and 1 of alcohol; or, if we double these numbers for the convenience of representing alcohol as a *binhydrate of etherine* (see p. 1274), 2 atoms of *anhydrous* sulphuric acid = 80, 4 of water = 36, and 2 of alcohol = 46; and are, in themselves, such as contain the elements of *sulphovinic acid*; so that we need only suppose them to be subjected to the proper temperature for that purpose; and not only is such *temperature* obtained by Mitscherlich's method of proceeding, but it is kept up during the experiment, and, at the same time, the continuous supply of alcohol furnishes materials for the constant formation of sulphovinic acid; and the sulphovinic acid (consisting of 2 atoms of anhydrous sulphuric acid, and 1 of alcohol, 46) is no sooner formed, than it is resolved into sulphuric acid, ether, and water; ether being formed by subtracting 2 atoms of anhydrous sulphuric acid and 1 atom of water from 1 atom of sulphovinic acid, or



It now only remains briefly to recapitulate the above statements, respecting the ultimate and proximate, or theoretical, composition of alcohol and ether, in order to see their mutual bearings: and for this purpose I have represented them in the following table. It must, however, be allowed that there are many points connected with the phenomena of etherification which are not adequately explained by any of the accepted theories; some of these are well discussed and illustrated in an Essay on the mutual action of chloride of zinc and alcohol by M. Masson. (*Ann. de Ch. et Ph.*, Lxix. 225.)

ALCOHOL.

				Equivalent Weights.						Equivalent Weights.			
		Atoms.						Atoms.					
Carbon	. . .	2	. . .	12		Carbon	. . .	4	. . .	24			
Hydrogen	. . .	3	. . .	3	or,	Hydrogen	. . .	6	. . .	6			
Oxygen	. . .	1	. . .	8		Oxygen	. . .	2	. . .	16			
<hr/>						<hr/>							
A Alcohol		1		23		B Alcohol		1		46			
<hr/>						<hr/>							
		Equivt. Atoms.		Weights.				Equivt. Atoms.		Weights.			
Carbon	2	. 12	} Olefiant gas	1	. 14	Carbon	4	. 24	} Etherine	1	. 28		
Hydrogen	2	. 2		} Water	1	. 9	Hydrogen	2		. 4	} Water	2	. 18
Do.	1	. 1					Do.	2		. 2			
Oxygen	1	. 8				Oxygen	2	. 16					
<hr/>						<hr/>							
c Alcohol		1		23		d Alcohol		1		46			
<hr/>						<hr/>							

ETHER.

	Atoms.	Equivalent Weights.
Carbon	4 . .	24
Hydrogen	5 . .	5
Oxygen	1 . .	8
E Ether	1	37

	Atoms.	Equivalent Weights.		Atoms.	Equivalent Weights.		Atoms.	Equivalent Weights.
Carbon	4 . .	24	} Olefiant gas	2 . .	28	Etherine	1 . .	28
Hydrogen	4 . .	4						
Do.	1 . .	1						
Oxygen	1 . .	8	} Water	1 . .	9	Water	1 . .	9
F Ether	1	37	Ether	1	37	Ether	1	37

ETHER.

ALCOHOL.

	Atoms.	Equivt. Weights.		Atoms.	Equivt. Weights.		Atoms.	Equivt. Weights.		Atoms.	Equivt. Weights.
Carbon	4 . .	24	} Ethule	1 . .	29	Carbon	4 . .	24	} Ether	1 . .	37
Hydrogen	5 . .	5				Hydrogen	5 . .	5			
						Oxygen	1 . .	8			
Oxygen	1 . .	8	} Oxygen	1 . .	8	Do.	1 . .	8	} Water	1 . .	9
						Hydrogen	1 . .	1			
G Ether	1	37	Ether	1	37	H Alcohol	1	46	Alcohol	1	46

A and B show the ultimate elements of *alcohol*, in reference to its single and to its double equivalent; C represents alcohol as a *hydrate of olefiant gas*, in reference to the equivalent A; and D as a *binhydrate of etherine*, in reference to the equivalent B; E shows the ultimate elements and equivalent of *ether*; F represents it as a *dihydrate of olefiant gas*, or as a *hydrate of etherine*; G exhibits ether as an *oxide of ethule*; and H alcohol as a *hydrated oxide of ethule*, or a *hydrate of ether*.

§ XXIII. COMBINATIONS OF ETHER, AND OF ETHERINE OR QUADRI-HYDROCARBON, WITH THE OXY-ACIDS.

I. OIL OF WINE. HEAVY OIL OF WINE. SULPHATIC ETHER. SULPHATE OF HYDROCARBON.—When the distillation of a mixture of sulphuric acid and alcohol is carried beyond the point at which ether ceases to come over, a portion of a liquid, looking like oil, is obtained, to which the above names have been applied; when washed, it has a bitter aromatic flavour. It has long been known under the name of *oil of wine*, and was formerly regarded as analogous in composition to the volatile oils. In endeavouring to determine the ultimate elements of this oil, by passing it over red hot oxide of copper, Mr. Hennell always obtained *sulphurous acid*, and a solution of sulphate of copper on washing the oxide he had used, notwithstanding every precaution had been taken to free the oil from all adhering acid. A few drops of the oil were added to a solution of chloride of barium, and gently heated, but no cloud was produced, although litmus paper indicated the presence of free acid; on evaporating the mixture, however, a precipitate fell as it became concentrated; and, on boiling to dryness, sulphate of baryta was found in the residue. It appeared, therefore, that the sulphuric acid was in some state of combina-

tion which prevented its usual action upon tests; or that its elements were in some peculiar state of arrangement in the oil of wine. Mr. Hennell made some experiments to determine the quantity of sulphuric acid thus elicited, from which it appeared, that 100 grains of the oil of wine afforded about 38 grains of *sulphuric acid*. His previous experiments had shown him that *hydrogen* and *carbon* were also elements of oil and wine; and, having determined their proportions by distillation through oxide of copper (adhering moisture and acid having been removed from the oil of wine by quicklime), he obtained from 100 grains (mean of several experiments) 8.30 hydrogen and 53.70 carbon; which appeared to indicate the composition of oil of wine to be 62 *hydrocarbon* + 38 *sulphuric acid*. It will be observed, that, as respects the carbon and hydrogen, the relative proportions nearly approximate to 6 and 1. Mr. Hennell observes, however, in regard to the above experiments, that we can only infer from them the composition of the *hydrocarbon combined with and neutralizing the sulphuric acid*; for that oil of wine dissolves a variable quantity of hydrocarbon, part of which separates in a crystalline form when the oil is kept for some time, or when exposed to cold. Having thus far determined the composition of oil of wine, its action upon heated solutions of chloride of barium, and chloride of potassium, was more particularly examined; it having been already observed, that in those cases an *acid* is evolved, which does not precipitate baryta. Two hundred grains of oil of wine were gently heated with 6 ounces of water for an hour; precipitated carbonate of baryta was then added, which dissolved, with effervescence, to the amount of 90 grains: the solution, filtered and set to evaporate, became acid, and deposited sulphate of baryta. The experiment, therefore, was repeated; but instead of *evaporating* the barytic solution, it was precipitated by carbonate of potassa, and filtered. The filtered solution, evaporated at a temperature not exceeding 150° , remained *neutral*, and afforded lamellar crystals, greasy to the touch, very soluble in water and alcohol, burning, when heated, with a flame like that of ether, and leaving an acid sulphate of potassa. To determine the composition of the crystals, 20 grains were heated to redness, and left a residue of 10.56 grains of sulphate of potassa, equal to 4.8 sulphuric acid, and 5.76 potassa. 20 grains were dissolved in a solution of caustic potassa, boiled to dryness, heated red hot, and, when cold, dissolved in distilled water; the excess of potassa was then saturated by nitric acid; and the solution added to one of chloride of barium; 28 grains of sulphate of baryta were obtained, nearly equal to 9.6 of sulphuric acid; the salt, therefore, contained *twice* the quantity of sulphuric acid required to form a neutral salt with the potassa, or *two proportionals*. The remaining elements of the salt were determined by heating it with oxide of copper, from which it appeared that the components of 100 grains are, potassa 28.84, sulphuric acid 48.84, carbon 13.98, hydrogen 2.34, water 7. These numbers may be considered as indicating:—

1	proportional of potassa	=	48
2	„ sulphuric acid	=	80
4	„ carbon	=	24
4	„ hydrogen	=	4

Mr. Hennell proceeds to show that the salts obtained from oil of wine are identical with the *sulphovينات* procured from the mixture of sulphuric acid and alcohol; the *sulphovinic acid*, therefore, must be regarded as a compound of 2 proportionals of sulphuric acid, and 1 of hydrocarbon, (consisting of 4 proportionals of carbon = 24, and 4 hydrogen = 4,) and corresponding, therefore, to the quadrihydrocarbon or *etherine*, above described (p. 547). This acid, however, has the property of neutralizing *single proportionals* only of bases; so that *one* proportional of the sulphuric acid appears to be neutralized by the hydrocarbon, furnishing an analogous instance to the *sulphonaphthalic acid* already mentioned (p. 553).

When *sulphovينات* are formed through the medium of *oil of wine*, a portion of quadrihydrocarbon is thrown off, amounting to half that which is contained in the oil; now, as oil of wine is a perfectly neutral compound, it may, in fact, be regarded as a sulphovinate of *etherine*, which in it performs the part of a base; and we may regard it as composed of

Sulphuric acid	2	.	.	80	.	.	2	.	.	80
Carbon	.	.	.	8	.	.	48	.	.	
Hydrogen	.	.	.	8	.	.	8	.	.	
} Etherine										
							2	.	.	56
<hr/>										
Oil of wine	1			136	or		1			136

Such is Mr. Hennell's view of the nature of *oil of wine*, and it obviously also includes that of sulphovinic acid, which he considers as a compound of sulphuric acid, with half the above quantity of hydrocarbon, or:—

Sulphuric acid	.	2	.	.	80	.	.	2	.	.	80
Carbon	.	.	.	4	.	.	24	.	.		
Hydrogen	.	.	.	4	.	.	4	.	.		
} Etherine											
							1	.	.	28	
<hr/>											
Sulphovinic acid		1			108		1			108	

Or if oil of wine be regarded as a sulphate of etherine ($4\text{ car} + 4\text{ h} + \text{sul}$), sulphovinic acid will be the bisulphate of the same base, or ($4\text{ car} + 4\text{ h} + 2\text{ sul}$).

The part which the sulphovinic acid performs in the generation of ether, I have already explained, and Mr. Hennell has shown, in the papers which I have quoted, not only that *ether* may be obtained from the sulphovinic acid as it exists in the sulphovينات, by combining its hydrocarbon with water, but also that, by doubling the water, it yields *alcohol*.

Serullas prepares this oil of wine as follows. (*Ann. de Ch. et Ph.*, xxxix. 153.) He distils a mixture of 1 part of alcohol, and 2·5 of concentrated sulphuric acid; a little ether is first formed, then a yellow oil, accompanied by an aqueous acid liquor; the oil is separated, washed in cold water, and then transferred to the receiver of the air pump, where it is placed by two capsules, the one containing sulphuric acid, the other fragments of potassa; in this way it gradually loses the sulphurous acid, water, alcohol, and ether, with which it was mixed in its original state. It then varies much in colour, becoming green and blue whilst in vacuo, but yellow when exposed to air; it has a penetrating aromatic odour,

and a cooling bitterish taste; it is soluble in alcohol and ether, but not in water; its specific gravity is 1.133.

On referring, however, to the analysis of this oil, as given by Serullas, Liebig, and Dumas, it evidently differs in composition from that examined by Hennell; Dumas, indeed, states that it was not obtained twice alike, but he presumes that it contains the true sulphate of hydrocarbon, or *sulphatic ether**, which, he says, should contain:—

				Dumas.
Sulphuric acid	1	40	51.9	51.6
Carbon	4	24	31.2	31.5
Hydrogen	5	5	6.5	6.8
Oxygen	1	8	10.4	10.1
Heavy oil of wine, sulphate of hydrocarbon, or, sulphatic ether }	1	77	100.0	100.0

The other characters of this oil are stated to be as follows: boiled with water, it is gradually converted into sulphovinic acid and alcohol, and an *oily hydrocarbon, lighter than water*; when the boiling is long continued, the whole of the sulphovinic acid is destroyed, and sulphuric acid, alcohol, and the light oil, are the products. Heated with alkaline solutions, the heavy oil of wine is converted into a sulphovinate; and the light oil, and probably alcohol, are given off. Potassium is not acted upon by it without heat, when sulphuret of potassium, and sulphate of potassa are formed.

LIGHT OIL OF WINE. ETHEROLE.—This, which is given off from the heavy oil in the above-mentioned processes, has a specific gravity = 0.917 to 0.920; it resembles olive oil. When shaken with water, and exposed in a cold place, it gradually deposits a crystallized substance, which, dried upon blotting paper, is tasteless, friable, aromatic when heated, specific gravity = .980, fusible at about 230° (110° Cent.), and volatile at 500° (260° Cent.).

There can be little doubt that this is the hydrocarbon of oil of wine, above analyzed by Hennell, and which Serullas also found composed of hydrogen and carbon in the ratio of 1 to 6.

SULPHOVINIC ACID.—The composition, production, and some of the properties of this acid have been necessarily included in my account of *ether*, and from the preceding statement, founded on Hennell's researches, it may be represented in its *anhydrous* state, as a compound of 2 atoms of sulphuric acid, and 1 of etherine.

Hydrated sulphovinic acid may be obtained by decomposing *sulphovinate of lead* or of *baryta* by sulphuric acid, or the former by sulphuretted hydrogen; it may be concentrated by the usual process in vacuo, taking care to avoid the production of sulphuric acid. In this state it is a colourless, sour liquid, specific gravity = 1.319; it is decomposed by a gentle heat; it dissolves in all proportions in water and alcohol, but is not soluble in ether; chlorine is apparently without action upon it, but nitric acid soon produces sulphuric acid in it; boiled with water it yields

* Dumas observes that it should properly be termed *sulphuric ether*, but to avoid the confusion that would arise in consequence of the application of that term to *ether*, he modifies it as above.

sulphuric acid and alcohol; all its salts are soluble, and most of them easily crystallizable; so that in reference to *hydrated sulphovinic acid* (containing 1 atom of anhydrous acid = 108 + 2 atoms of water = 18) it would appear to be formed by the action of 4 atoms of protohydrated, or common liquid sulphuric acid, upon 2 atoms of alcohol ($23 \times 2 = 46$) in such a way that 2 atoms of anhydrous sulphuric acid unite to the elements of the 2 atoms of alcohol, whilst the remaining 2 atoms of sulphuric acid become bihydrated. Thus we have $4(s' + q) + 2(2car + 3h + o)$ producing $(2s' + 4car + 6h + 2o) + 2(s' + 2q)$. Here again hydrated sulphovinic acid presents itself as a sulphate of alcohol, or as a compound of 2 atoms of sulphuric acid, 1 of quadrihydrocarbon, and 2 of water. These statements are therefore as follows:—

Sulphuric acid	2	. . .	80	} 1 atom anhydrous sulphovinic acid 108 2 atoms water . 18	} 126
Carbon	4	. . .	24		
Hydrogen	6	. . .	6		
Oxygen	2	. . .	16		
<hr/>						
Hydrated sulphovinic acid		1		126		

Or,

Sulphuric acid . . .	2 . . .	80 . . .	2 . . .	80 . . .	2 . . .	80
Carbon	4 . . .	24	} Etherine 1 . . .	28	} Alcohol 2 . . .	46
Hydrogen	4 . . .	4				
Do.	2 . . .	2	} Water . 2 . . .	18		
Oxygen	2 . . .	16				
<hr/>						
Hydrated sulpho- vinic acid } . . .	1 . . .	126	1 . . .	126	1 . . .	126

The above statements respecting the composition of oil of wine, sulphovinic acid, ether, and alcohol, may be simplified by considering those compounds as sulphates and hydrates of etherine; thus,

Etherine	$4car + 4h$
Oil of wine	$4car + 4h + sul'$
Sulphovinic acid	$4car + 4h + 2sul'$
Ether	$4car + 4h + q$
Alcohol	$4car + 4h + 2q$

SULPHOVINATES.—We are indebted for the first accurate analysis of these curious salts to Mr. Hennell; they are soluble in water, and many of them in alcohol, by which they are separable from their corresponding sulphates. When heated they are decomposed with varying phenomena, dependent upon the temperature to which they are submitted, and the nature of the base. At a high temperature they burn, and leave a carbonaceous residue, containing a bisulphate, or a mixture of a sulphate and sulphuric acid. Only a few of the sulphovينات have been minutely described, but they are an interesting class of salts, and some of them highly deserving further examination: the *sulphovinate of ammonia* especially deserves to be studied.

The *sulphovينات* are generally obtained by heating a mixture of equal weights of alcohol and sulphuric acid, and when cold diluting and saturating it with carbonate of lime, baryta, or lead, when soluble sulphovينات, and insoluble sulphates of those bases are formed, and may be

separated by filtration and crystallization. From these salts the other sulphovinates may be obtained, either by double decomposition by the soluble sulphates, or by liberating the sulphovinic acid by sulphuric acid, and then saturating with the required bases.

SULPHOVINATE OF POTASSA. ($P + \text{sulv'}$).—This salt, which has already been adverted to, forms micaceous crystals, like those of hydrated boracic acid; of a greasy feel and bitter taste. From its composition above given, together with its water of crystallization, it appears to contain:—

Potassa	1	48	29.1	1	48
Sulphuric acid	2	80	48.5	Sulphovinic acid	108
Etherine	1	28	17.0		
Water	1	9	5.4		
<hr/>					
Crystallized sulpho- vinate of potassa	1	165	100.0	1	165

SULPHOVINATE OF SODA ($S + \text{sulv'}$) yields efflorescent crystals of a bitter taste, soluble in 2 of cold and 1 part of boiling water, and containing 1 atom of soda, 1 of sulphovinic acid, and 3 of water.

SULPHOVINATE OF BARYTA ($B + \text{sulv'}$) forms permanent square tabular crystals, readily soluble in water and insoluble in alcohol, containing,

Baryta	1	77	36.3
Sulphovinic acid	1	108	51.0
Water	3	27	12.7
<hr/>			
Crystallized sulphovinate of baryta	1	212	100.

When this salt is dried in vacuo or at a temperature of 164° , it loses 1 atom of its component water.

SULPHOVINATE OF LIME. ($C + \text{sulv'}$).—By slow evaporation this salt forms quadrilateral tables, very soluble in water and alcohol, and of a slightly sweet taste; and which by desiccation in vacuo lose 2 atoms of their constituent water: when cautiously distilled it yields oil of wine. This salt consists of

Lime	1	28	17.2	Sulphate of lime	1	68	41.7
Sulphovinic acid	1	108	66.2	Sulphuric acid	1	40	24.5
Water	3	27	16.6	Etherine	1	28	17.2
<hr/>				Water	3	27	16.6
<hr/>							
Crystallized sulpho- vinate of lime	1	163	100.0		1	163	100.0

SULPHOVINATE OF LEAD. ($Pl + \text{sulv'}$).—This salt forms a deliquescent saline mass (VOGEL), silky crystals (DUMAS), extremely soluble both in water and alcohol.

SULPHOVINATE OF COPPER ($Cu + \text{sulv'}$), formed by dissolving carbonate of copper in sulphovinic acid, yields large blue tabular crystals, very soluble in water, and soluble in alcohol. It is not precipitated by chloride of barium: when heated a little above 212° , as when long boiled in water, it passes into sulphate of copper. This salt is easily formed by

adding sulphate of copper to sulphovinate of baryta. It probably contains 3 atoms of water. (DUMAS.)

III. ETHEROSULPHURIC ACID. ETHIONIC ACID. ($\text{ETH} + 2 \text{S}'$).—When the vapour of anhydrous sulphuric acid is slowly introduced into absolute alcohol, kept at a low temperature, an oleaginous liquid is formed, and no gas evolved: if too little alcohol has been used, crystals of sulphuric acid form, which redissolve when alcohol is added. The liquid when mixed with water does not heat, and on saturating the solution with baryta, abundance of sulphate of baryta is formed, together with a soluble salt of baryta, which must be evaporated in vacuo. This salt contains sulphuric acid, but it is not sulphovinate of baryta, for it is neither soluble in alcohol nor crystallizable; nor does it yield oil of wine when distilled. It contains, according to Magnus (*Ann. de Ch. et Ph.*, lii. 155),

Sulphuric acid	2	80	41.2
Baryta	1	77	39.7
Carbon	4	24	12.4
Hydrogen	4	4	2.1
Water	1	9	4.6
Ethionate of baryta	1	194	100.0

According to Magnus, the acid contained in this salt is constituted of

Sulphuric acid	2	80	68.4
Etherine	1	28	23.9
Water	1	9	7.7
Ethionic acid	1	117	100.0

It is, therefore, a hydrated bisulphate of etherine; whilst sulphovinic acid is an anhydrous bisulphate of etherine; or it is an anhydrous bisulphate of ether ($2 \text{S}' + 4 \text{CAR} + 5 \text{H} + \text{O}$).

By partially decomposing ethionic acid by heat, Magnus obtained an isomeric acid, which has been termed *isæthionic acid*: the salt which it forms with baryta, resembles the ethionate of that base in ultimate composition, but differs from it in its properties.

According to Dumas, the existence of these distinct acids, namely, the sulphovinic, ethionic, and isothionic, resulting from the mutual action of sulphuric acid and alcohol, was anticipated by Sertuerner, under the terms of *protethionic*, *deutethionic*, and *tritethionic* acids. (*Ann. de Ch. et Ph.*, xiii. 62.)

IV. PHOSPHOVINIC ACID. ETHEROPHOSPHORIC ACID.—It was ascertained many years ago by Boullay, that phosphoric acid might be substituted for sulphuric, in the formation of ether, and Lassaigne found that an acid analogous to the sulphovinic was so formed; the further investigation of this subject has been pursued by Pelouze and by Liebig. (*Ann. de Ch. et Ph.*, lii. 37, and liv. 31.)

Etherophosphoric Acid is obtained by the careful decomposition of the etherophosphate of baryta by sulphuric acid, or of the etherophosphate of lead by sulphuretted hydrogen; it is concentrated, first by ordinary evaporation, and then in vacuo. It is then of an oleaginous consistence, colourless, inodorous, very sour, and soluble in water, alcohol, and ether, in all proportions. When much diluted it is not decomposed by con-

tinued boiling; but when concentrated, a temperature of 212° gradually resolves it into ether, alcohol, hydrocarbon, and a mixture of phosphoric acid and charcoal. Its concentrated solution affords crystals: it coagulates albumen; and has the same properties whether prepared from phosphoric or from paraphosphoric acid. When diluted it dissolves zinc with effervescence, and expels carbonic acid from its combinations, forming salts which for the most part are soluble. Pelouze regards this acid as analogous to the sulphovinic in its atomic composition, or as a compound of phosphoric acid and alcohol; but from Liebig's analysis it appears to consist of phosphoric acid and ether, and, therefore, resembles the ethionic acid.

The crystallized *etherophosphate of baryta* includes 12 atoms of water, which may be expelled by heat, and the *anhydrous* etherophosphate remains; although this salt has been analyzed by Pelouze and Liebig, the results are not satisfactory as relates to the composition of the acid.

V. NITROUS ETHER. HYPONITROUS ETHER.—The production of an ethereal fluid by the mutual action of nitric acid and alcohol is said to have been remarked by Paracelsus and afterwards by Kunckel, but it was forgotten till rediscovered by Navier, in 1742. (NAVIER and GEOFFROY, *Mém. de l'Acad. de Paris*, 1742.) It was subsequently studied by Thenard (*Mém. d'Arcueil*, i. 75, and 359), and more recently by Dumas and Boullay. (*Ann. de Ch. et Ph.*, xxxvii. 19.)

Many processes have been published for the preparation of this ether (see DUMAS, *Ch. app. aux Arts*, v. 553, and THOMSON, *Inorg. Chem.*, ii. 317); among them the following, suggested by Thenard, is the least objectionable. Introduce into a sufficiently capacious tubulated retort equal weights of alcohol (specific gravity .820) and of nitric acid of commerce (specific gravity 1.30), and connect it with five Wolfe's bottles, the first of which is empty, and the remaining four half-filled with a saturated solution of salt in water. Apply a gentle heat to the retort, till the liquor begins to effervesce; then withdraw the fire, and the vapour passing through the bottles, which should be kept cold by a mixture of ice and salt, deposits the ether upon the saline solution. In performing this experiment, the retort should not be more than one-sixth filled with the mixture of acid and alcohol; and cold water or other means should be at hand to cool it, if required, in order to subdue the violence of the effervescence. The alcohol should be first poured in, and then the acid, and not mixed by agitation. If the materials are warm, the acid fuming, and the alcohol of proper strength, the action often begins immediately upon mixture, with a cracking noise, escape of air-bubbles, and great effervescence, so that, notwithstanding the size of the retort, its contents are very apt to pass over into the first receiver, and it is often burst; this may generally be prevented by applying a wet cloth to the retort. The tubes through which the vapour is to pass should not be too small, for, in consequence of the suddenness and abundance of its extrication, it requires a ready means of escape: indeed, the whole process requires much management and caution, and is most successful when conducted upon rather a small scale in a large retort; with from 1 to 2 ounces of alcohol and acid for instance.

When the effervescence has entirely ceased, the residue in the retort is found to be equal in bulk to less than one-third of the materials employed: the first bottle contains an acid mixture of alcohol, water, and nitrous ether; but the bulk of the ethereal product is found upon the cold saline solution of the second bottle; a little also passes into the third bottle. The ethereal products are collected, digested with powdered lime, and redistilled into a receiver cooled by ice: not more than 100 parts of *rectified ether* are usually obtained from 1000 of the mixture of acid and alcohol.

Besides the ether, many other products are the result of this operation, such as nitrogen and its oxides, nitrous acid, carbonic acid, and traces of acetic acid and acetic ether: oxalic acid sometimes is found in the contents of the retort.

Nitrous ether has the following properties. It has a slightly yellow tint, and a peculiar odour, which, when much diffused, is not unlike that of ripe apples; its specific gravity 0·880 at 40°. It is extremely volatile, boiling under mean pressure at a temperature of about 70°, so that at summer heat it is apt, on removing the stopper of a bottle containing it, to evaporate very rapidly, and even to enter into spontaneous ebullition: dropped upon the hand it instantly disappears and excites great cold; it is very inflammable, burning with a yellowish flame, and leaving no perceptible residue; when recent, it has no action on litmus, but in a few days it becomes perceptibly sour, especially in the presence of moisture and light. Mixed with water, a part is dissolved, and another part decomposed, forming nitric acid, and giving off nitrous gas; mixed with solution of potassa it soon forms hyponitrite of potassa, alcohol, and traces of acetate of potassa. It is without action on ammonia.

There are various modes of viewing the composition of this and similar ethers: as concerns ultimate components, they are as follows:—

				Dumas and Boullay.	
Carbon	4	24	32·00	32·69	
Hydrogen	5	5	6·67	6·85	
Oxygen	4	32	42·67	41·46	
Nitrogen	1	14	18·66	19·00	
<hr/>				<hr/>	
Nitrous ether	1	75	100·00	100·00	

These elements are equivalent to

Ethule	1	29	38·7	} Ether	1	37	49·4
Oxygen	1	8	10·7				
Hyponitrous acid	1	38	50·6		1	38	50·6
<hr/>				<hr/>			
Nitrous ether	1	75	100·0	or	1	75	100·0

Or they may be represented by

Olefiant gas	2	28	37·3	} Etherine	1	28
Water	1	9	12·0		1	9
Hyponitrous acid	1	38	50·7		1	38
<hr/>				<hr/>		
Nitrous ether	1	75	100·0		1	75

It is obvious, from the preceding statement, that this ether may be theoretically regarded either as a *hyponitrite of oxide of ethule* ($eth + o$

+ \bar{n}), or as a *hyponitrite of ether* ($\text{ETH} + \bar{n}$), or as a *hydrated hyponitrite of etherine* ($\text{ethn} + \bar{n} + q$). The composition of the other ethers of this class admits of similar hypothetical representation; the simplest view of the subject is that which regards them as *salts of the oxide of ethule*, or *combinations of ether with the acids*.

VI. OXALIC ETHER.—This compound was discovered by Bergman (*Opusc. Chim. Phys.*, i.); it was afterwards examined by Thenard (*Mém. d'Arcueil*, ii. 11), and its principal properties shown by Dumas and Boullay in their excellent researches on ethers. (*Ann. de Ch. et Ph.*, xxxvii. and liv.) It is prepared by distilling 1 part of alcohol, 1 of oxalic acid, and 2 of sulphuric acid; alcohol and sulphuric ether pass over, and then an oil-like liquid which collects at the bottom of the receiver, and which is *oxalic ether*: it must be separated from the supernatant liquid, and poured into a glass of water; it often floats at first, but as the sulphuric ether which it contains gradually evaporates, it falls in drops to the bottom. On adding the alcohol in the receiver, or a fresh portion of alcohol to the residuary contents of the retort, a fresh portion of oxalic ether may be obtained, and this may even be repeated a third time: the different portions of oxalic ether thus obtained are mixed, and purified by boiling with powdered litharge, till its boiling point attains 360° (183° or 184° Cent.), when it becomes stationary: performing this operation in a flask with a short neck, the water, sulphuric ether, and alcohol, pass off in vapour, and the excess of acid is retained by the oxide of lead; the oxalic ether is then decanted into a clean dry retort and redistilled.

Oxalic ether, thus prepared, is of specific gravity = 1.0929 at 45° : it boils at 360° , at mean pressure, yielding a vapour of low tension, the density of which is 5.08: its odour is aromatic, with a slight taint of garlic or phosphorus; it is soluble in alcohol and ether, and very sparingly so in water. When dry, it may be long preserved without decomposition; but when humid, it is soon resolved into oxalic acid and alcohol; the hydrated alkalis immediately effect this change, becoming oxalates, and evolving alcohol. It consists of:—

					Dumas and Boullay.		
Carbon	6	36	49.31	49.7	= Carbon vapour	3	2.53
Hydrogen	5	5	6.85	6.5	= Hydrogen gas	5	0.34
Oxygen	4	32	43.84	43.8	= Oxygen gas	2	2.22
Oxalic ether	1	73	100.00	100.0	= Vapour of oxalic ether	1	5.09

Or, it may be represented as

Ether	1	37	50.69	{ Etherine . . . 1 . . . 28 . . . 38.36			
				{ Water . . . 1 . . . 9 . . . 12.32			
Oxalic acid	1	36	49.31	Oxalic acid	1	36	49.31
Oxalic ether	1	73	100.0	Oxalic ether	1	73	100.00

Hence we have ($6\text{ car} + 5\text{ h} + 4\text{ o}$) = ($\text{ETH} + \text{ox}'$) = oxalic ether. The conversion of this ether into alcohol and oxalic acid, by the action of hydrated potassa or soda, depends upon the combination of the ether with an atom of water, at the moment of its evolution; or assuming oxalic

ether to be a hydrated oxalate of etherine, it is equally obvious that an additional atom of water would convert the etherine into alcohol.

When a current of dry ammoniacal gas is passed into anhydrous oxalic ether, heat is evolved, and a solid compound is at length formed, which, dissolved in boiling alcohol and filtered, yields silky crystals on cooling. The same compound may be obtained, according to Liebig (*Ann. de Ch. et Ph.*, Liv. 225 and Lv. 125), by mixing oxalic ether with an alcoholic solution of ammonia; the mixture yields crystals, on spontaneous evaporation. To the substance thus obtained, Dumas has applied the name *oxaméthane*. It is colourless, fusible, volatile, soluble in alcohol, soluble in cold water, but converted by boiling into acid oxalate of ammonia. Liquid ammonia immediately converts it into *oxamide*. This substance consists, according to Dumas, of 1 atom of oxalic ether, and 1 atom of ammonia; so that its ultimate elements are

Carbon . . .	6 . . .	36	} = Oxalic ether 73	} = Oxaméthane 90
Hydrogen . . .	5 . . .	5		
Oxygen . . .	4 . . .	32		
Nitrogen . . .	1 . . .	14	} = Ammonia . 17	
Hydrogen . . .	3 . . .	3		

These elements are equivalent to

Carbon . . .	2	. . .	12	} = Oxamide . . 44
Hydrogen . . .	2	. . .	2	
Oxygen . . .	2	. . .	16	
Nitrogen . . .	1	. . .	14	} = Alcohol . . 46
Carbon . . .	4	. . .	24	
Hydrogen . . .	6	. . .	6	
Oxygen . . .	2	. . .	16	

Hence it is, that when aqueous ammonia and oxalic ether are mixed and agitated together, a white precipitate falls, consisting of pure oxamide.

According to Ettling a *carbonate of oxide of ethule* (carbonic ether) is formed during the action of potassium on oxalic ether. (*Jour. de Pharm.*, xix. 17.)

VII. OXALOVINIC ACID.—When a solution of oxalic ether in anhydrous alcohol is mixed with a similar solution of potassa, in such proportion as to saturate half the acid contained in the ether, crystals are soon deposited, which are almost insoluble in absolute alcohol, and which consist of *oxalovinate of potassa*. This salt is soluble in water, and is not affected by a temperature of 212°; it is anhydrous, and consists of 1 atom of oxalate of potassa, and 1 atom of oxalic ether. It may be decomposed by dissolving it in weak alcohol, filtering the solution to separate a little oxalate of potassa which falls, and then carefully adding sulphuric acid, by which sulphate of potassa is formed and precipitated, and oxalovinic acid set free. It decomposes the carbonates of lime and of baryta, and forms soluble oxalovinates; the pure acid may easily be obtained from the *oxalovinate of baryta*. Many bases, among which is the oxide of copper, decompose this acid, and produce oxalates. When its aqueous solution is evaporated, even with the utmost caution, oxalic acid remains, and the oxalovinic acid disappears. The oxalovinic acid appears to consist of 2 atoms of oxalic acid, and 1 atom of etherine.

VIII. FORMIC ETHER.—Distill 7 parts of dry and pulverized *formiate of soda*, with 10 of sulphuric acid, and 6 of anhydrous alcohol; agitate the product, first with a little magnesia to separate acid, and then with water to abstract alcohol; lastly, deprive it of water and of residuary traces of alcohol by the action of chloride of calcium. (DÖBEREINER, *Ann. de Ch. et Ph.*, liii. 105.) Formic ether is colourless, and has somewhat of an hydrocyanic odour. Its specific gravity is = 0.915 at 65°. It boils at 132°. It requires 9 parts of water at 65° for solution, and when long boiled with water, especially if potassa be present, it is resolved into alcohol and formic acid. This ether has not been satisfactorily analyzed.

IX. CHLOROCARBONIC ETHER.—When absolute alcohol is admitted into a balloon, containing chlorocarbonic acid gas, it becomes warm and yellowish; when the action has terminated, air is admitted, and soon after, the liquid may be poured out and mixed with about its volume of distilled water; two layers are presently formed, the one of an oil-like liquid, the other lighter, and containing free hydrochloric acid. The oily liquor, abstracted by a pipette, and rectified over chloride of calcium and litharge, in a water bath, has the following properties. It is a colourless liquid, without action on litmus; its odour is peculiar and irritating; it boils at about 200°; its specific gravity = 1.133 at 60°. It consists of

Carbon	6	36	33.0
Hydrogen	5	5	4.6
Oxygen	4	32	29.4
Chlorine	1	36	33.0
<hr/>			
Chlorocarbonic ether	1	109	100.0

Dumas, from whom I have made the preceding abstract (*Chim. app. aux Arts*, v. 570; *Ann. de Ch. et Ph.*, liv. 225), considers this ether as including a new acid. When it is mixed with liquid ammonia, violent action ensues, hydrochlorate of ammonia is formed, and a new product, called by Dumas *uréthane*, is formed; it is obtained by evaporating the mixture in vacuo to dryness, and distilling it in a dry retort heated by an oil bath; a colourless liquid passes over, which concretes into a white crystalline matter, like spermaceti, and sal-ammonic remains in the retort.

Urethan is white, fusible, and volatile when dry, without decomposition; but, when moist, ammonia is plentifully evolved; it is readily soluble in water and in alcohol, and the solution is neutral. It consists of

				Dumas.
Carbon	6	36	41.0	
Hydrogen	7	7	7.3	
Oxygen	4	32	36.0	
Nitrogen	1	14	15.7	
<hr/>				
Urethan	1	89	100.0	

These elements are equivalent to 2 atoms of carbonic acid ($2(car + 2o)$), 1 atom of ammonia ($n + 3h$), and 1 of etherine ($4car + 4h$). There are various other views which may be taken of it, and among them, it may be regarded as consisting of 1 atom of *carbonic ether*, or hydrated

carbonate of etherine $= (4car + 4h) + (car + 2o + q)$ and 1 atom of urea $= (car + 2h + o + n)$. This formula has led Dumas to the term *urethan*.

X. ACETIC ETHER. (ETH + ac'.)—This ether was discovered as far back as 1759 by the Count de Lauraguais. It may be prepared by distilling a mixture of 63 parts of concentrated acetic acid, and 17 of sulphuric acid, with 100 of alcohol; the receiver should be carefully cooled; 125 parts may be distilled over. Another process consists in distilling 3 parts of acetate of potassa, 3 of absolute alcohol, and 2 of sulphuric acid, to dryness. The product is mixed with a fifth part of sulphuric acid, and by careful distillation, acetic ether equal in volume to the alcohol may be obtained. The results of these operations, contain free acid and alcohol; the former may be abstracted by lime or chalk, and the latter by chloride of calcium.

Acetic ether boils at 105° ; it is lighter than water, and has a peculiarly agreeable odour; it burns with a yellowish flame, and acetic acid is developed by its combustion. Water dissolves about one seventh of its weight of this ether, and the solution is decomposed by potassa, giving rise to an acetate and to alcohol. Ammonia has no action upon it. Acetic ether is composed of

Carbon	8	48	54.55	54.820
Hydrogen	8	8	9.09	8.755
Oxygen	4	32	36.36	36.425
Acetic ether	1	88	100.00	100.000

These elements are equivalent to

Etherine	1	28	31.8	} Ether	1	37	42
Water	1	9	10.2				
Acetic acid	1	51	58.0		1	51	58
Acetic ether	1	88	100.0		1	88	100

The density of the vapour of acetic ether is 3.06, which corresponds with

	Vols.	Sp. Gr.
Carbon vapour	2	1.66
Hydrogen	4	0.24
Oxygen	1	1.11
Vapour of acetic ether	1	3.01

According to Pelouze, when carbonic acid is passed through an alcoholic solution of acetate of potassa, acetic ether and bicarbonate of potassa are formed; this is a curious instance of etherification at common temperatures; the insolubility of the bicarbonate in alcohol is probably concerned in the action.

Acetal. When alcohol contained in a saucer is covered by an open jar, and some moistened spongy platinum placed in watch glasses just above its surface, acid vapour is formed, which is absorbed by, or falls into, the alcohol, and gradually renders it very sour; if it be then distilled off powdered chalk, and rectified over chloride of calcium, *acetal* (or *oxidized ether* of Döbereiner) is obtained. It is a colourless fluid, the odour of which resembles that of nitrous ether. Its specific gravity is 0.842. It boils at 167° . It dissolves in alcohol and ether, and in

about 6 parts of water. It burns with a bright flame. By potassa, and by sulphuric acid, it is converted into a yellow resin. By the action of spongy platinum it forms acetic acid. (LIEBIG, *Pogg. Ann.*, xxvii. 605.) It appears to consist of

consist of				Dumas.
Carbon	8	48	59.26	59.7
Hydrogen	9	9	11.11	11.3
Oxygen	3	24	29.63	29.0
Acetal	1	81	100.00	100.0

XI. BENZOIC ETHER (ETH + *ben'*) was discovered by Scheele; it may be obtained by subjecting a mixture of 4 parts of alcohol, 2 of benzoic acid, and 1 of hydrochloric acid to distillation; when about half has passed over, it is returned into the retort, and the distillation is repeated in the same way two or three times. The *ether* is chiefly contained in the residue; it is washed with water, and then carefully distilled off finely powdered protoxide of lead. (THENARD, *Mém. d'Arcueil*, ii. 8.) Its specific gravity is 1.0539 at 50°; its boiling point, 408° = 209° Cent.; its tension very feeble.

A curious case of the production of this ether has been noticed by Wöhler and Liebig. (*Ann. de Ch. et Ph.*, li. 299.) When chloride of benzule and alcohol are mixed, the temperature of the mixture rises so as to produce ebullition, hydrochloric acid is evolved, and on adding water to the residue, an oil-like substance separates, which is benzoic ether.

Benzoic ether consists of

ether consists of					Dumas.
Carbon	18	108	72.0	72.40	
Hydrogen	10	10	6.7	6.57	
Oxygen	4	32	21.3	21.03	
<hr/>					
Benzoic ether	1	150	100.0	100.00	

These elements are equivalent to 1 atom of ether + 1 atom of benzoic acid.

XII. SUCCINIC ETHER. (ETH + *suc'*).—Dumas, upon the authority of F. D'Arcet, gives the following process for preparing this ether. Distill together 10 parts of succinic acid, 20 of alcohol, and 5 of concentrated hydrochloric acid, cohobating the distilled product four or five times; the residue in the retort will then consist of alcohol, water, succinic and hydrochloric acid, and succinic ether; when mixed with water, the succinic ether separates like heavy oily drops; it is collected, washed with cold water, boiled in a flask with a short neck, till its boiling point becomes constant, and lastly, distilled off dry protoxide of lead.

Succinic ether is a limpid, colourless, oily liquid, of an aromatic odour; it boils at 417° (214° Cent.); its specific gravity is 1.036. It is resolved by potassa into succinic acid and alcohol. Chlorine decomposes it under the influence of light, and forms crystals which have not been examined. This ether consists of 1 atom of ether + 1 of succinic acid, or of

Carbon	8	48	55.2
Hydrogen	7	7	8.0
Oxygen	4	32	36.8
Succinic ether	1	87	100.0

XIII. TARTARIC ETHER may be obtained from 5 parts of tartaric

acid, 7 of alcohol, 2 of sulphuric acid; distill the mixture till a little sulphuric ether begins to be formed. If at this period we withdraw the heat, the liquor assumes a syrupy consistence; but water does not separate the compound of the vegetable acid and alcohol. By adding, by degrees, solution of potassa, we throw down bitartrate of potassa; then, after having just saturated the redundant acid, if we evaporate the liquid, and treat it in the cold with very pure alcohol, we obtain, by evaporation of the alcoholic solution, a substance which, on cooling, becomes like syrup. This substance has a brown colour, and a bitter and nauseous taste. It is void of smell and acidity, and is soluble in water and alcohol. It does not precipitate solution of chloride of calcium, but copiously that of chloride of barium. When heated it diffuses dense fumes, which have the odour of garlic, and at the same time it leaves a residue, not alkaline, containing much sulphate of potassa. If distilled with potassa, it is resolved into a very strong alcohol, and much tartrate of potassa; it is, therefore, an ethereal combination analogous to the preceding. (THENARD, *Mem. d'Arcueil*, ii. 13.)

XIV. TARTROVINIC ACID.—When pulverized tartaric acid is digested for six hours with its weight of anhydrous alcohol at a temperature between 150° and 160° , and then diluted with 4 parts of water, gently heated, and saturated by carbonate of baryta, tartrate of baryta falls, and the solution, evaporated at about 110° and filtrated, yields, on spontaneous evaporation, crystals of tartrovinic acid. This salt, when decomposed by an equivalent of dilute sulphuric acid, filtered, and evaporated in the dry vacuum, leaves a white inodorous residue, which is *tartrovinic acid*: it has a sweetish acid taste, crystallizes in long oblique prisms, deliquescent, soluble in water and in alcohol, insoluble in ether, and burning with a pale flame; boiled for some hours with 40 parts of water, it is resolved into tartaric acid and alcohol. Subjected to a temperature of between 300° and 400° , it fuses and is decomposed, yielding alcohol, water, acetic ether, acetic acid, carbonic acid, carburetted hydrogen, a volatile oil, and a liquid resembling pyroacetic spirit; and a mixture of charcoal, pyrotartaric acid, and oily matter, remains in the retort.

Tartrovinic acid is decomposed when heated with nitric or sulphuric acid; it dissolves iron and zinc with the evolution of hydrogen; it has no action on tin.

The aqueous solution of tartrovinic acid dropped into baryta water, forms a precipitate, which gradually diminishes as the liquid approaches neutralization, and again increases on adding excess of the acid; this is not the case with tartaric acid; nitric acid redissolves the precipitates. Tartrovinic acid does not precipitate any solution of strontia; added to lime water, it throws down a precipitate soluble in excess of acid; it forms no precipitate under any circumstances, either with potassa or soda. With neutral acetate of lead it forms small nacreous prismatic crystals, insoluble in tartrovinic acid, but soluble in nitric acid. With a saturated solution of nitrate of silver it gives an insoluble precipitate. These characters distinguish the tartrovinic from the tartaric acid. (GUERIN-VARRY, *Ann. de Ch. et Ph.*, lxii. 55.) Its ultimate components in its anhydrous state, as in the salts of silver and baryta, are

				Guérin-Varry.
Carbon	12 . .	72 . .	42.6 . .	43.07
Hydrogen	9 . .	9 . .	5.3 . .	5.27
Oxygen	11 . .	88 . .	52.1 . .	51.66
<hr/>				
Anhydrous tartrovinic acid	1	169	100.0	100.00

The crystallized acid consists of

Anhydrous tartrovinic acid	1 . .	169 . .	95
Water	1 . .	9 . .	5
<hr/>			
Crystallized tartrovinic acid	1	178	100

The components of the anhydrous acid are therefore equivalent to 2 atoms of tartaric acid (66×2) and 1 atom of ether (37); and those of the crystallized acid are equivalent to 2 atoms of tartaric acid, 1 of ether, and 1 of water; the former, therefore, is an anhydrous and the latter a hydrated bitartrate of ether.

THE SALTS OF THE TARTROVINIC ACID (*tartrovinates*) are soluble in water and in hydrated alcohol, and sparingly soluble in anhydrous alcohol; they are mostly crystallizable, greasy to the touch, and burn with a flame resembling that of alcohol. They fuse when heated to between 380° and 420° , and are decomposed at a temperature a little above that of their point of fusion; the products of their decomposition are water, alcohol, acetic ether, acetic acid, a volatile oil, carburetted hydrogen, and carbonic acid, and charcoal remains in the retort mixed, if the temperature has not been too high, with a pyrotartrate. Boiled in water the tartrovinates are resolved into water, alcohol, and acid tartrates. Heated with an alkali to between 320° and 340° they evolve alcohol, acetic ether, and a bitter oil. With the exception of the tartrovinat of silver, they all contain water of crystallization, which may be abstracted by a dry vacuum. In the neutral tartrovinates, the oxygen in the acid is to that in the base as 11 to 1. When anhydrous, they may be regarded as compounds of 2 atoms of anhydrous tartaric acid, 1 of ether, and 1 of base. They are obtained either by double decomposition, or by the mutual action of tartaric acid, alcohol, and a carbonate.

Tartrovinat of Potassa is obtained by the decomposition of tartrovinat of baryta, by slight excess of sulphate of potassa; evaporate the filtrated solution nearly to the consistence of syrup, and throw down undecomposed sulphate of potassa by alcohol, filter again and evaporate spontaneously. It is a white, inodorous, bitterish salt, and crystallizes in truncated rhomboidal prisms; it is soluble in about its own weight of water at 60° , and in all proportions at 212° . This salt consists of

				Guérin-Varry.
Potassa	1 . .	48 . .	21.2 . .	20.83
Tartrovinic acid	1 . .	169 . .	74.8 . .	75.17
Water	1 . .	9 . .	4.0 . .	4.00
<hr/>				
Crystallized tartrovinat of potassa	1	226	100.0	100.00

There is also a *basic tartrovinat of potassa*, alkaline to reagents, and which crystallizes in octagonal prisms with polyhedral terminations, apparently resulting from an oblique base.

Tartrovinat of soda is prepared as the salt of potassa; it forms

rhomboidal and rectangular lamellar crystals, which include $2\frac{1}{2}$ atoms of water.

Tartrovinat of lime is prepared as the salt of baryta; it forms white rectangular and lamelliform prisms, including 5 atoms of water of crystallization.

Tartrovinat of baryta. The preparation of this salt is described above; its primary form is the oblique rhomboidal prism; it is white, inodorous, and slightly bitter; its crystals include 2 atoms of water; 100 parts of water, at 60° , dissolve about 36 of this salt, and at 212° , 128 parts. It is insoluble in anhydrous alcohol.

Tartrovinat of zinc is produced by the action of the dilute acid on zinc; it is white, and crystallizes in rectangular prisms, greasy to the touch.

Tartrovinat of copper is formed by digesting oxide of copper in warm tartrovinic acid; it forms groups of silky prisms, including 6 atoms of water.

Tartrovinat of silver is thrown down in the form of minute prismatic crystals, on mixing concentrated solutions of nitrate of silver, and of tartrovinat of potassa or baryta, the latter being in excess. The precipitate must be dried in the dark at a temperature not exceeding 120° , after having been washed with cold water, in which it is very sparingly soluble; it becomes red, and afterwards brown, when exposed to light. It consists of

					Guérin-Varry.	
Oxide of silver	. .	1	. .	116	. .	40.7
Tartrovinic acid	. .	1	. .	169	. .	59.3
						40.44
						59.56
Tartrovinat of silver		1		285		100.0
						100.00

PARATARTROVINIC ACID. RACEMOVINIC ACID.—The action of the paratartaric acid on alcohol corresponds with that of the tartaric, and the resulting paratartrovinic acid, as well as the salts which it forms, bear a general analogy to the corresponding tartrovinates. The composition of the paratartrovinic acid may be represented by 2 atoms of paratartaric acid, 1 of ether, and 2 of water. (GUERIN-VARRY, *Ann. de Ch. et Ph.*, lxii. 73.)

XV. CITRIC ETHER.—When a hot saturated solution of citric acid, mixed with alcohol, hydrochloric acid, and a certain proportion of sulphuric ether, is kept for six or eight hours at a temperature between 125° and 135° , and then water added, citric ether separates in the form of an oil-like liquid. Its formation in this way is uncertain, and its properties have not been examined. (PELOUZE.)

§ XXIV. COMBINATIONS OF ETHULE WITH HALOGENS, OR OF ETHERINE WITH THE HYDRACIDS.

I. HYDROCHLORIC ETHER. MURIATIC ETHER. CHLORIDE OF ETHULE.

—*Sweet or dulcified spirit of salt*, was a favourite preparation with the alchemists; they conceived it to possess some peculiar solvent powers in regard to salts of gold: it was also used in medicine; it was prepared in various ways; either by distilling a mixture of alcohol and hydrochloric acid; or of chloride of sodium, sulphuric acid, and alcohol.

Hydrochloric ether may be obtained by subjecting to careful distillation a concentrated solution of hydrochloric acid gas in alcohol; or a mixture of 1 part of alcohol, 1 of sulphuric acid, and 2 of fused and finely-powdered chloride of sodium; or a mixture of chloride of antimony, or of tin, and alcohol. In all these cases, hydrochloric ether passes over; it should first be transmitted into warm water, by which its adhering acid and alcohol are abstracted, and its vapour may then be condensed by conducting it through a cold tube, and receiving it in a bottle surrounded by ice and salt.

Hydrochloric ether, thus condensed, is a limpid, colourless liquid, of a peculiar penetrating odour, and a sweetish flavour; it is neutral; its specific gravity = 0.874 at 42°: it has not been congealed; it boils at about 60°; the specific gravity of its vapour is 2.219. It burns with a flame tinged with green, and exhales the fumes of hydrochloric acid. Mixed with 4 volumes of oxygen and detonated by the electric spark, it yields 2 volumes of carbonic acid; it is very slowly altered by water and by alkalis. Passed through a red-hot tube, it is decomposed into hydrochloric acid, hydrocarbon, charcoal, and hydrogen. Its formula is ($4\text{ car} + 5\text{ h} + \text{c}$) or ($4\text{ car} + 4\text{ h} + \text{hc}'$); its components being

Carbon	. . . 4	. . . 24	. . . 36.9	. . . Dumas.
Hydrogen	. . . 5	. . . 5	. . . 7.7	. . . 37.73
Chlorine	. . . 1	. . . 36	. . . 55.4	. . . 7.70
				. . . 54.57
Hydrochloric ether	1	65	100.0	100.00

These elements are equivalent to

Ethule	. . . 1	. 29	. 35.43		Etherine	. . . 1	. 28	. 43.1
Chlorine	. . . 1	. 36	. 54.57	or,	Hydrochloric acid	. 1	. 37	. 56.9
Hydrochloric ether	1	65	100.00		Hydrochloric ether	1	65	100.0

II. CHLORAL.—The mutual action of *chlorine* and alcohol was originally inquired into by Scheele and Westrumb; it afterwards engaged the attention of the principal chemists who have expounded the theory of etherification, and has been more recently investigated by Liebig and by Dumas. (*Ann. de Ch. et Ph.*, xlix. 146; lvi. 113.) The resulting product was originally termed *heavy muriatic ether*; the term *chloral* (referring to chlorine and alcohol) has been applied to it by the last-mentioned chemists. Chloral is obtained by passing a large quantity of chlorine, carefully dried, through anhydrous alcohol; the alcohol is at first kept cold, but when the first action is over, it requires to be gradually warmed; during the whole operation, which lasts several hours, hydrochloric acid gas is evolved, and must be allowed to escape. Liebig found that several days were required to complete this action upon a quantity of alcohol, amounting to about 8 ounces. The product of this operation is mixed with twice its bulk of sulphuric acid, and subjected to careful distillation; a limpid oil-like liquid passes over, which is to be heated in an open flask till its boiling-point attains about 200°; it should then again be distilled off sulphuric acid, and finally rectified off a small quantity of fresh quick-lime, the distillation being performed in a bath of salt and water.

Chloral is a transparent colourless liquid, of a greasy aspect; its specific gravity at 65° is 1.502, its boiling point $= 206^{\circ}$; and the density of its vapour about $= 5.0$. It has an irritating odour, is almost tasteless, somewhat caustic in its action upon the skin, soluble in water, neutral, and its solution is not affected by nitrate of silver. If, instead of dropping the chloral into water, and heating it to effect the solution, it be put into the contact of a few drops of water, the liquids combine into a white crystalline solid, and heat is evolved; and when a few drops of chloral are put into a flask containing humid air, small groups of crystals gradually form upon its interior; these are *hydrate of chloral*. When chloral is poured upon sulphuric acid, and left to itself, it forms a white substance, which Liebig calls *insoluble chloral*. Chloral dissolves iodine, bromine, sulphur, and phosphorus. When its vapour is passed over heated lime or baryta, those bases become incandescent, carbonic oxide is evolved, and metallic chlorides mixed with carbon remain. This sometimes happens in rectifying chloral over quicklime. The hydrated alkaline oxides decompose chloral; nitric acid is almost without action upon it. Chloral consists of

				Dumas.
Carbon . .	4 . .	24 . .	16.11 . .	16.6
Hydrogen .	1 . .	1 . .	0.67 . .	0.7
Oxygen . .	2 . .	16 . .	10.74 . .	10.8
Chlorine .	3 . .	10 . .	72.48 . .	71.9
<hr/> Chloral	<hr/> 1	<hr/> 149	<hr/> 100.00	<hr/> 100.0

Hydrate of chloral consists of 1 atom of chloral and 1 of water.

I must refer to Dumas (*Chim. app. aux Arts*, v. 608) for details of the theory of the various changes which alcohol undergoes during the action of chlorine, and the formation of chloral. The term *chloric ether* is sometimes applied to chloral, and sometimes to the chloride of hydrocarbon, described at page 543.

Chloroform. Soubeiran and Liebig, by distilling chloral mixed with lime and water, or with solution of potassa, obtained a liquid, which when shaken with sulphuric acid, and then separated, and rectified over baryta, in a perfectly dry retort, yielded a dense limpid fluid, which has been designated *chloroform*. The same compound is obtained more easily by distilling a mixture of 1 pound of chloride of lime, 3 of water, and 3 ounces of alcohol, in a capacious retort; about 3 ounces of chloroform pass over.

The specific gravity of chloroform is 1.480 at 65° : its boiling point about 140° : the density of its vapour $= 4.2$. It is decomposed when passed over red-hot iron and copper, and, when passed through a red-hot glass tube, deposits crystals, apparently of chloride of carbon. Chloroform consists of

				Dumas.
Carbon . .	2 . .	12 . .	9.9 . .	10.24
Hydrogen .	1 . .	1 . .	0.9 . .	0.83
Chlorine .	3 . .	108 . .	89.2 . .	88.93
Chloroform	1	121	100.0	100.00

III. HYDRIODIC ETHER. IODIDE OF ETHYLE. ($4car + 5h + i$).—This compound was discovered by Gay Lussac. (*Ann. de Ch. et Ph.*, ix.

89.) It is best obtained by mixing in a retort, 4 parts of iodine, 10 of alcohol of 0·833, and gradually adding 2·5 of phosphorus: when the greater part has distilled over, 3 parts more of alcohol are put into the retort, and the distillation carried to dryness; the product is washed with cold water, and the ether rectified over chloride of calcium.

Hydriodic ether is colourless; it has a penetrating ethereal odour; its specific gravity at 74° is 1·92. It boils at 148° , and the density of its vapour is 5·409. It is not inflammable, but when dropped on red-hot charcoal it diffuses purple vapour. It is decomposed when passed through a red-hot tube, and among the products is an unctionous matter containing iodine. Exposed to air, hydriodic ether becomes red. It is sparingly soluble in water, but readily so in alcohol. Potassium does not decompose it; alkalis, nitric acid, and chlorine, only slowly act upon it; sulphuric acid rapidly decomposes it. It consists of

Carbon . . .	4 . .	24 . .	15·58
Hydrogen . .	5 . .	5 . .	3·25
Iodine . . .	1 . .	125 . .	81·17
<hr/>			
Hydriodic ether	1	154	100·00

or, of 1 atom of etherine + 1 hydriodic acid.

Iodoform is a compound analogous to *chloroform*, and obtained by a similar process; its formula is ($2\text{car} + h + 3i$). (SERULLAS and DUMAS, *Ann. de Ch. et Ph.*, lvi. 133.)

IV. HYDROBROMIC ETHER. BROMIDE OF ETHULE. ($4\text{car} + 5h + b$.)

To prepare this ether, introduce into a tubulated retort 40 parts of alcohol, specific gravity ·827, and 1 of phosphorus, then add, gradually and carefully, 7 to 8 parts of bromine. The bromide of phosphorus which is formed, decomposes the water of the alcohol, and produces hydrobromic and phosphorous acids: distill by a gentle heat into a cooled receiver. When the distilled product is mixed with water, hydrobromic ether separates and falls to the bottom; if acid, it must be washed with a dilute solution of potassa.

Hydrobromic ether is colourless, transparent, heavier than water, of a strong ethereal odour, and a pungent taste; it is very volatile, soluble in alcohol, and precipitated by water; it has not been analyzed, but probably, like its associates, consists of 1 atom of etherine + 1 hydrobromic acid, or 1 atom of ethule + 1 bromine.

Löwig prepares hydrobromic (bromic) ether by decomposing ether by bromine; he purifies it by redistillation off lime. When boiled with a solution of potassa *bromoform* is evolved, and formiate and bromide of potassium are produced.

BROMOFORM.—Bromide of lime, distilled with water and alcohol, yields a product analogous to chloroform, which has been termed *bromoform*. (DUMAS, *Ann. de Ch. et Ph.*, lvi. 113.)

V. HYDROCYANIC ETHER. CYANURET OF ETHULE. ($4\text{car} + 5h$) + ($2\text{car} + n$).—When equal parts of cyanuret of potassium and sulphovinate of baryta are heated in a retort, a product is obtained, which,

when washed with water, agitated with and then distilled off powdered chloride of calcium, yields *hydrocyanic ether*. (PELOUZE, *Jour. de Phar.*, xx.) In this operation, the water contained in the sulphovinate is decomposed, its oxygen is transferred to the potassium of the cyanuret, and its hydrogen to the cyanogen to produce *hydrocyanic acid*, which, with the *hydrocarbon* of the sulphovinate, forms this ether.

Hydrocyanic ether is colourless and has a strong alliaceous odour; its specific gravity is 0.70° , it boils at 180° . When pure it does not affect a solution of nitrate of silver, and it is with difficulty decomposed by solution of potassa. It dissolves in all proportions in alcohol and in ether. It is sparingly soluble in water. It consists of

Carbon	6	36	65.5
Hydrogen	5	5	9.1
Nitrogen	1	14	25.4
<hr/>			
Hydrocyanic ether	1	55	100.0

This ether is poisonous, but much less so than hydrocyanic acid.

VI. SULPHOCYANIC ETHER.—By distilling a mixture of 1 part of sulphocyanuret of potassium, 2 of sulphuric acid, and 3 of anhydrous alcohol, Liebig obtained a compound consisting apparently of sulphuret of cyanogen and etherine. (*Ann. de Ch. et Ph.*, xli. 202.)

VII. SULPHURET OF ETHULE ($4\text{ car} + 5\text{ h} + \text{s}$) is obtained by passing the vapour of chloride of ethule through an alcoholic solution of protosulphuret of potassium: chloride of potassium is precipitated, and the liquid contains sulphuret of ethule, which separates on the addition of water; its density is 0.815 ; it has an alliaceous odour; it boils at 153° .

VIII. HYDROSULPHURIC ETHER. HYDROSULPHATE OF HYDROCARBON. HYDROSULPHURET OF SULPHURET OF ETHULE. MERCAPTAN. (ZEISE, *Ann. de Ch. et Ph.*, xxxv. 87.)

When sulphovinate of baryta is distilled with a concentrated solution of sulphuret of barium, an ethereal liquid passes over, whilst the sulphovinate becomes a sulphate; this liquid floats upon the water; it is to be washed and digested upon powdered chloride of calcium. It is then colourless, combustible, and has an odour resembling assafœtida. It is separable by careful distillation into two compounds; the most volatile, hitherto little examined, has been termed *thiolic ether* (from *θειον*, sulphur), and the other *mercaptan* (from *mercurio aptum*), in consequence of its high attraction for mercury. Dumas regards the latter as a *binhydrosulphate of hydrocarbon*. This compound is best obtained by decomposing the *mercaptide of mercury* by sulphuretted hydrogen.

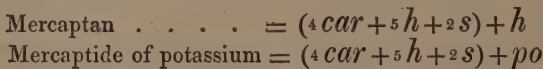
Mercaptan is a colourless liquid, of an extremely penetrating alliaceous odour, and a peculiar sweetish taste; its specific gravity is 0.842 at 60° : its boiling point about 144° . It does not congeal at -8° , nor does it redden litmus; it dissolves in all proportions in alcohol and ether, and is sparingly soluble in water. Its alcoholic and aqueous solutions occasion copious lemon-coloured precipitates in solution of acetate, but not of nitrate of lead. It acts powerfully on peroxide of mercury, water is generated, and a colourless crystalline compound, peculiarly constituted,

is the result. In the same way, it decomposes the perchloride of mercury, forming the same product, with the formation of hydrochloric acid. This crystalline compound, when subjected to the action of sulphuretted hydrogen, gives rise to the reproduction of the original ether, or mercaptan, and to bisulphuret of mercury, and nothing else. It consists, according to Zeise, of

Carbon	4	24	38.7
Hydrogen	6	6	9.7
Sulphur	2	32	51.6
Mercaptan	1	62	100.0

Now it is obvious that these elements may be regarded as constituting a true ether, or ethereal salt, composed of 1 atom of etherine = ($4\text{ car} + 4\text{ h}$) + 2 atoms of sulphuretted hydrogen $2(\text{s} + \text{h})$, so that it corresponds with the other hydracid ethers, except that it contains 2 atoms, instead of 1, of sulphuretted hydrogen or hydrosulphuric acid.

But Zeise regards mercaptan as the *hydruret* of a compound base, which he terms *mercaptum*; this base, therefore, is presumed to consist of ($4\text{ car} + 5\text{ h} + 2\text{ s}$). When mercaptan is acted on by potassium, hydrogen is evolved, and a *mercapturet* or *mercaptide of potassium* is formed. So that mercaptan and mercaptum bear a relation to each other and to other bodies, analogous to cyanogen and hydrocyanic acid.



So that mercaptum (*mercaptule*?) is a bisulphuret of ethule.

IX. SELENIURET OF ETHULE ($4\text{ car} + 5\text{ h} + \text{se}$) is formed, according to Löwig, by distilling seleniuret of potassium with sulphovinate of lime or potassa.

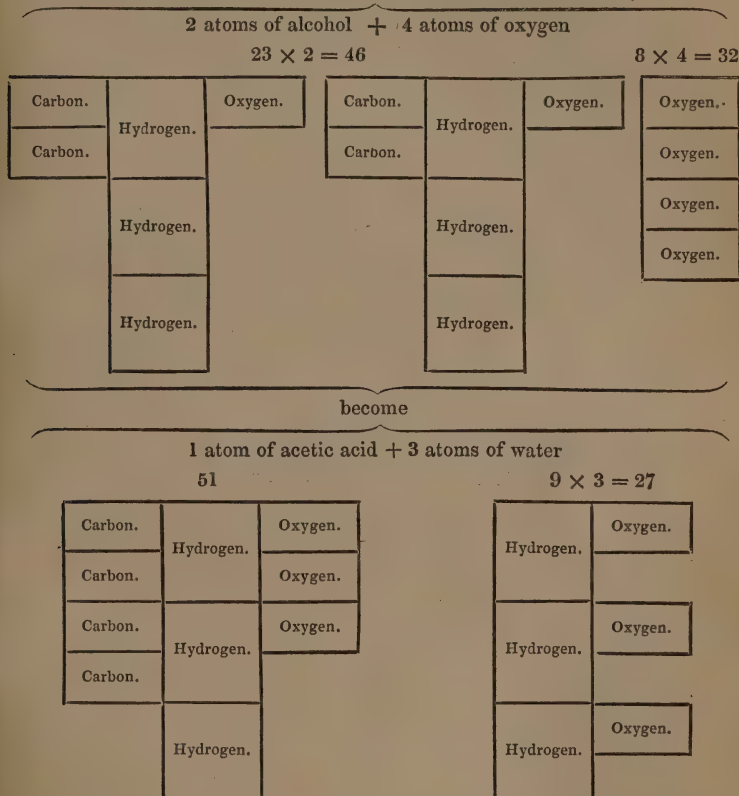
§ XXV. ACETOUS FERMENTATION. VINEGAR. ACETIC ACID. METHYLENE. ALDEHYD.

WHEN any spirituous or vinous liquor, such as wine, or beer, in which vinous fermentation has ceased, is exposed to the access of air, and to a due temperature (above 65°) a new fermentation ensues, in which oxygen is absorbed, carbonic acid evolved, and the alcohol gradually passes into *acetic acid*, which is composed of

				Prout.	Berzelius.	Gay Lussac and Thenard.
Carbon	4	24	47.06	47.05	46.83	50.224
Hydrogen	3	3	5.88	5.88	6.35	5.629
Oxygen	3	24	47.06	47.07	46.82	44.147
Acetic acid	1	51	100.00	100.00	100.00	100.000

It will be recollected that *alcohol* consists of ($2\text{ car} + 3\text{ h} + \text{o}$). When, therefore, 1 atom of alcohol has the whole of its hydrogen abstracted (by the action of the absorbed oxygen from the air), the remaining elements (which are $2\text{ car} + \text{o}$), added to another atom of unchanged alcohol ($+\text{o}$), produce *acetic acid*. If, therefore, we set out with *two* atoms of alcohol,

and abstract half their hydrogen, we shall convert them, with the addition of 1 atom of oxygen, into 1 atom of *acetic acid*: now this abstraction of hydrogen is in some way induced by the presence of the oxygen of the atmosphere, so that the 2 atoms of alcohol become in fact converted into 1 atom of acetic acid, and 3 atoms of water, as shown in the following diagrams:—



It is evident, therefore, that the evolution of *carbonic acid* which attends acetous fermentation, is not essential to the formation of acetic acid, and is probably referable to the decomposition of a portion of undecomposed sugar, or other matter contained in the liquor, which is susceptible of *vinous* fermentation; or that it may in some cases arise from other changes, or from the decomposition of a portion of the acetic acid itself. The quantity of carbonic acid evolved during the change of wine into vinegar is usually small and very variable, and not one of the leading phenomena, as is the case in vinous fermentation*.

* The conversion of alcohol into acetic acid independent of the formation of carbonic acid, is said to ensue during the action of the black precipitate, produced by alcohol in sulphate of platinum (platinum-black) upon the vapour of alcohol.

A mere mixture of alcohol and water will not undergo acetous fermentation, without the presence of yeast, gluten, or some analogous substance; hence the more perfect wines do not become sour, even when exposed to air, because they contain no ferment.

Although in this mode of producing acetic acid, alcohol is its common source, there are other vegetable substances from which it may be obtained, independent of *vinous* fermentation; as from certain mucilaginous and amylaceous solutions containing vegetable albumen; and when once acetic acid is present, it hastens acetic fermentation, hence the necessity of great cleanliness in regard to the casks and vessels used in vinous fermentation, and in the preservation of wine and beer: sour yeast, paste, and similar substances in incipient decomposition, are also great promoters of acetification.

The action of yeast and similar substances in the conversion of alcohol into vinegar, that is, in causing it to absorb oxygen, is referred by Liebig to a process resembling that by which sulphurous is converted into sulphuric acid by the action of nitric oxide: the ferment, it is presumed, absorbs oxygen from the atmosphere and transfers it to the alcohol; but the ferment itself gradually changes and becomes insoluble in water. "Some ascribe the acetification of alcohol to a new process called *catalysis*, by which mere contact is supposed to cause combinations and decompositions; but the same explanation would apply to the action of nitric oxide in the production of sulphuric acid, were it not that the visible formation and decomposition of nitrous acid betray the real nature of the change: there is, therefore, no occasion to assume a new and mysterious power, as it is evident that the organic matters alluded to induce acetification, as the powder of platinum does by absorbing and condensing oxygen so as to enable the alcohol to combine with it."

VINEGAR.—This term is applied to the *dilute acetic acid*, which is chiefly employed for domestic consumption, and which varies extremely in strength, flavour, and composition, according to the sources whence it is obtained. In wine countries it is procured by exposing weak wines to the access of air at a due temperature, and its strength, flavour, and colour, depend upon the characters of the wine employed. In this country beer-vinegar is sometimes used, or a *wort* is prepared for the purpose, and, in these cases, the product acquires peculiarities dependant upon the foreign matters necessarily present. A good extemporaneous vinegar may be made by dissolving 1 part of sugar in 6 parts of water, and adding 1 of brandy or other strong spirituous liquor, and a little yeast: this mixture is put into a sufficiently large cask, with the bung-hole left open, and exposed to a temperature of between 70° or 80°; in a month or six weeks, the clear vinegar may be drawn off. Liebig recommends 100 parts of water, 13 of brandy, 4 of honey, and 1 of tartar; or 120 of water, 12 of brandy, 3 of brown sugar, 1 of tartar, and $\frac{1}{2}$ of sour dough, left for some weeks in a warm place, as good ingredients for the production of vinegar.

The production of acetic acid by the slow combustion of alcohol has been above alluded to; Mitscherlich compares its formation by the exposure of alcohol, water, and a ferment, to air, to that process, and alludes

to the mode of forming it sometimes practised, which consists in suffering a mixture of 1 part of alcohol and 8 or 9 of water, with a little yeast, to trickle through beech shavings previously soaked in vinegar, and lying loosely in a cask perforated full of holes; he says that the air loses so much oxygen, that if collected as it issues from the upper holes, it extinguishes flame, and that the temperature of the liquid rises to 85° , when that of the atmosphere is only 60° ; that by the first operation, half the alcohol is acetified, and that the acetification is complete by a repetition of the process, provided it be slowly conducted; and that vinegar may be made in this way in a few hours.

In all these cases, the principle of acetification is the same, and consists in the formation of alcohol, and its subsequent conversion into acetic acid by the abstraction of hydrogen, as above explained. Air must always, therefore, have access; but the vessels should not be too open, because in that case acid is lost by evaporation, as the temperature is necessarily high. Vinegar is apt to be infested by flies (*Musca cellaris*), and by animalcules, commonly termed eels (*Vibrio aceti*): these may be destroyed by passing it through a spiral tube immersed in water heated to 212° , or by heating it in a hot-water bath. When vinegar is exposed to air, it gradually becomes turbid, or *molhery*, losing its acidity, and depositing a slippery gelatinous substance, which, when collected and dried, resembles gum, and is destitute of nitrogen; it does not, therefore, resemble animal mucus, to which it is sometimes compared. The vinegar becomes weak and mouldy as these changes go on, and they are rapid in proportion to its weakness.

The vinegar of commerce is very various as to strength, and before the present method of producing it from *pyroligneous acid*, which I shall immediately describe, was brought into practice, it was generally adulterated with other acids, especially the sulphuric, a fraud detected by the production of a precipitate insoluble in nitric acid, on the addition of acetate of baryta. Vinegar is also sometimes sharpened by hydrochloric acid, when it gives a precipitate, likewise insoluble in nitric acid, with nitrate of silver. These precipitates require to be tested, in regard to their insolubility in nitric acid, because they are thus distinguished from other combinations of baryta and of oxide of silver, produced by the other acids or substances present in genuine vinegar, but small traces of sulphates are found in almost all vinegars, and these must be allowed for in using the barytic test. If nitric acid be present in vinegar it changes the colour of a weak solution of indigo, when boiled with it. Pepper, and other acrid substances, are rendered evident by carefully neutralizing the vinegar with carbonate of soda, when they are detected by their undisguised pungency.

The specific gravity of vinegar depends more upon the foreign matters which it contains than upon its actual strength, so that its value cannot be judged of by that criterion: the density of the best vinegar (commonly called *white-wine* vinegar), is about 1.020 to 1.025. To ascertain the proportion of *real acetic acid* which it contains, it must be cautiously neutralized by carbonate of soda (dry or crystallized), and the quantity of that salt requisite for the purpose indicates the proportion of real acetic acid present, 54 parts of *dry* carbonate of soda being equivalent to 51 of

true or anhydrous acetic acid. The equivalent of *carbonate of lime*, which is 50, is so near that of acetic acid, as to furnish a ready mode of ascertaining the value of vinegar or other dilute acetic acid; for this purpose a piece of clean white marble is selected and accurately weighed. it is then suspended by a thread in a proper quantity of the vinegar to be examined, which is occasionally cautiously stirred, so as to mix its parts without chipping the marble; when it is no longer acted on, it is removed, washed, dried, and weighed; its loss is equivalent to the acetic acid. Another mode of ascertaining the strength of vinegar consists in neutralizing it by hydrate of lime; acetate of lime is extremely soluble, so that the quantity of acetate of lime formed and dissolved, is directly as the quantity of acid present, and the *density* of the resulting solution of acetate of lime, is in the same ratio. (See Messrs. J. and P. TAYLOR on an *Acetometer*. *Quart. Jour.*, vi.) A solution of ammonia, of known strength, blued by litmus, may sometimes conveniently be used as a neutralizing acetometric fluid. "An ounce of good vinegar should saturate about 30 to 32 grains of pure and dry carbonate of potassa; such vinegar contains about 5 per cent. of anhydrous acetic acid, and its density is from 1.01 to 1.03." (LIEBIG.)

DISTILLED VINEGAR.—When vinegar is subjected to careful distillation, the first portion which comes over usually contains a little alcohol; this is followed by dilute acetic acid, which, towards the end of the process, especially if distilled over an open fire, acquires an empyreumatic odour: the residue is brown, very acid, and has a burned flavour. According to Mr. R. Phillips (on the *London Pharmacopœia*, p. 7), when the best English malt-vinegar, of the specific gravity 1.0204, is distilled, the first eighth part which passes over is of the specific gravity 0.99712, so that it contains a little alcohol; a fluid-ounce of it, = 1.8047 cubic inches, dissolves from 4.5 to 5 grains of precipitated carbonate of lime: the next six-eighths have the specific gravity 1.0023, and a fluid-ounce dissolves 8.12 grains of the carbonate; a fluid-ounce of the acid, of specific gravity 1.007, dissolves 15 to 16 grains of precipitated carbonate of lime, or 13.8 grains of marble.

Distilled vinegar is colourless, and wants the agreeable fresh flavour and odour of the original vinegar, compared with which it is flat: this arises partly from a trace of alcohol and of acetic ether which it contains, and also from a peculiar organic matter which passes over in distillation, and which distilled vinegar sometimes deposits in the form of a gray sediment; its nature is unknown: when the acid containing it is neutralized by an alkali and slowly evaporated, it communicates a brown tinge, in consequence of the action of the air upon it. If vinegar has been distilled from a copper still, through a pewter worm, it is always more or less contaminated by copper, lead, or tin, and consequently becomes discoloured when tested by sulphuretted hydrogen, especially after it has been reduced in bulk by evaporation. Earthenware, or even silver condensing-tubes, are therefore used by the wholesale vinegar-distillers; or upon the small scale, glass vessels may be employed; but the use of distilled vinegar is now almost entirely superseded by that of a mixture of pure acetic acid and water, and this mixture, coloured by burned sugar, is pretty generally employed as a substitute for vinegar.

When vinegar is subjected to a low temperature its aqueous part is that which first congeals, and the remaining unfrozen portion is the strongest; in this way vinegar may, to a certain extent, be concentrated.

PYROLIGNEOUS ACID.—The production of *vinegar* by the destructive distillation of wood, has already been mentioned as one of the numerous discoveries of Glauber* (p. 27). It is now conducted upon a large scale, expressly for obtaining that acid. For this purpose the following apparatus is used. A series of cast-iron cylinders, about 4 feet in diameter, and 6 feet long, are built horizontally in brick-work, so that the flame of one furnace may play round about two cylinders, both ends of which project a little from the brick-work. One of them has a disc of cast iron well fitted and firmly bolted to it, from the centre of which disc an iron tube about 6 inches diameter proceeds, and enters at a right angle the *main* tube of refrigeration. The diameter of this tube may be from 9 to 14 inches, according to the number of cylinders. The other end of the cylinder is called the mouth of the retort. This is closed by a disc of iron, smeared round its edge with clay-lute, and secured in its place by wedges. The charge of wood for such a cylinder is about 8 cwt. The hard woods, oak, ash, birch, and beech, are alone used, and these should be *seasoned* or kept for some time to become dry. Fir does not answer†. The heat is kept up during the day-time, and the furnace is allowed to cool during the night. Next morning the mouth is opened, the charcoal removed, and a new charge of wood is introduced. The average produce of crude vinegar, called *pyroligneous acid*, is 35 gallons. It is much contaminated with tar; is of a deep-brown colour; and has a

* Berzelius justly observes that this acid was probably known at a much more remote period, and used by the Egyptians in the process of mummification; he quotes the following passage from Pliny in favour of this opinion. (*Hist. Nat.*, lib. xvi., p. 2.) “*Pix liquida in Europa e teda (Pinus silvestris) coquitur, navalibus muniendis, multosque alios ad usus. Lignum ejus concisum, furnis, undique igne extra circumdato, fervet; primus sudor, aquæ modo, fluit canali; hoc, in Syria, cedrum vocatur, cui tanta est vis, ut in Ægypto, corpora hominum defunctorum, eo perfusa, servantur.*” See, in reference to this subject, what I have above said respecting *Kreasote* (p. 1167).

† In reference to this subject, it appears from Stoltze's experiments, that the dried wood of all trees yields nearly the same quantity of fluid product when similarly distilled, but that the proportion of acetic acid in it is very variable. The following table illustrates this:—

100 parts of dry wood yield	Acid Liquor.	1 ounce of which saturates grains of Carbonate of Potassa.	Empyreumatic Oil.	Charcoal.
Birch, (<i>Betula alba</i>)	45	55	8·60	24·4
Beech, (<i>Fagus sylvatica</i>) . . .	44	54	9·55	24·6
Oak, (<i>Quercus robur</i>)	43	50	9·06	26·2
Ash, (<i>Fraxinus excelsior</i>) . . .	46·8	44	8·80	22·1
White poplar, (<i>Populus alba</i>) .	45·8	39	8·05	23·4
Wild plum, (<i>Prunus padus</i>) . .	43·7	37	10·35	21·6
Juniper, (<i>Juniperus communis</i>) .	45·8	29	10·73	22·7
Spruce fir, (<i>Pinus abies</i>) . . .	41·2	29	13·70	21·2
Scotch fir, (<i>Pinus sylvestris</i>) .	42·4	28	11·80	21·5

specific gravity of 1.025. Its total weight is therefore about 300 lbs. But the residuary charcoal is found to weigh no more than one fifth of the wood employed. The crude pyroligneous acid is rectified by a second distillation in a copper still, in the body of which about 20 gallons of viscid tarry matter are left from every 100. It has now become a transparent brown vinegar, having a considerable empyreumatic smell, and a specific gravity of 1.013. Its acid powers are superior to those of the best household vinegar, in the proportion of 3 to 2. (URE's *Dictionary*, Art. ACID, *acetic*.)

The purification of this crude acid is generally effected as follows; it is saturated with slaked lime, previously made into a thin cream with water; in this way much of the empyreumatic extractive is precipitated in insoluble combination with the lime; the clear solution, containing acetate of lime, is then drawn off and mixed with a concentrated solution of sulphate of soda, till no further precipitation of sulphate of lime ensues; when this has fallen, the supernatant liquor is let off, the residuary sulphate washed, and the whole of the solution evaporated; during this process, empyreumatic resin separates upon the surface, and is skimmed off, and when the solution has acquired a due density, it is set aside to crystallize, and the mother-liquor is poured off and treated as before. At last, a brown uncrystallizable liquid remains, which contains, besides acetate of soda, an empyreumatic extractive, and resin combined with soda, and which may be decomposed by evaporation to dryness, and calcination, so as to leave the soda. The crystallized salt, which is impure acetate of soda, after having been purified by solution and recrystallization, is fused in an iron pot, stirred till it dries, and the heat is then carefully raised to incipient carbonization, by which the empyreumatic matters which rendered it impure are carbonized, whilst the salt itself, if the operation be skilfully conducted, is little damaged; the mass is then dissolved in water, filtered, and recrystallized, and yields pure *acetate of soda*. This salt is then distilled with 0.36 of its weight of sulphuric acid, either in glass, or in metallic stills with silver condensers. The product is a strong acid, of the specific gravity 1.05; it still has an empyreumatic flavour, which is removed by well-burned animal charcoal; it is then duly diluted with water, and applicable to all the purposes for which common vinegar is employed; when intended for the table, it is coloured by burned sugar, and flavoured by a few drops of acetic ether. For pickles and sauces of all kinds, it is generally used in a somewhat stronger state than common vinegar. It is used as a substitute for vinegar in all the processes of the arts, being more or less purified in these cases, according to the purposes for which it is required.

ACETIC ACID.—Pure acetic acid, or as it was formerly called, *radical vinegar*, is obtained by decomposing acetate of soda; this salt is first purified by two or three solutions and crystallizations, and then carefully desiccated, by heating and stirring it, without fusion, in an iron basin; it is then pulverized, and put into a capacious tubulated retort, with two equivalents of pure sulphuric acid, at a temperature of about 125°; acetic acid is liberated, but when about an eighth part has passed over, the retort must be carefully heated; the distillation may be continued till the

saline matter in the retort, which is bisulphate of soda, is in quiet fusion. The products of this first distillation must be rectified over a little dried acetate of soda, then placed in ice till it congeals; the congealed acid is suffered to drain by inverting the bottle which contains it, and in that frozen state it may be regarded as pure hydrated acetic acid; it retains its solid form till the thermometer rises to about 50° ; if cooled down to 45° , and then shaken, or a particle of solid matter dropped into it, it congeals, and at the same time an immersed thermometer rises to 51° . Its crystals are generally flat plates of a pearly lustre; it has a strong irritating odour, agreeable when much diluted, and is powerfully acid and caustic, reddening the skin, and raising a blister. It absorbs moisture from the air, and dissolves in all proportions in water and in alcohol. The specific gravity of this acid (the liquified crystallized acid) is 1.06296 at 60° , but its density is no criterion of its strength, as shown in the following table, drawn up by Dr. Thomson, according to whom the crystalline or glacial acid consists of 1 atom of anhydrous acid + 1 atom of water.

Atoms of Acid.		Atoms of Water.		Sp. Gr. at 60° .		Atoms of Acid.		Atoms of Water.		Sp. Gr. at 60° .
1	+	1	.	1.06296		1	+	6	.	1.06708
1	+	2	.	1.07060		1	+	7	.	1.06349
1	+	3	.	1.07084		1	+	8	.	1.05974
1	+	4	.	1.07132		1	+	9	.	1.05794
1	+	5	.	1.06820		1		10	.	1.05439

The liquid acid, therefore, is at its greatest density when it consists of 1 atom of anhydrous acid, and 4 atoms of water, or of about 100 of real acid and 72 of water. It appears, also, that the density of the acid containing only 1 atom of water, is nearly the same with that containing 7 atoms.

Acetic acid has not been obtained in an uncombined anhydrous state. When heated, it distils over without change. It is only partially decomposed by a red heat, yielding acetone and carbonic acid: at a very high temperature it is resolved into inflammable gases and carbon. If passed over red-hot charcoal, it yields carbonic acid, water, carbonic oxide, and carburetted hydrogen.

Cold acetic acid is unflammable, but when heated, its vapour burns with a blue flame; the oxyacids are almost without action upon it. Chlorine, under ordinary circumstances, little affects it, but exposed to it under the direct solar rays, hydrochloric and chlorocarbonic acids are formed, and crystalline chloracetic acid.

Acetic acid is displaced from its combinations by most other acids. It forms a well-defined class of salts, *acetates*, all of which are soluble in water, and in which the oxygen in the acid is to that in the base as 3 to 1. Some of the peroxides convert part of this acid into carbonic acid and water, by which they are reduced to a soluble state, and form protacetates. It is a solvent of many organic products, among which are camphor, resins, and albumen.

The composition and equivalent of the anhydrous acetic acid have been above given; the crystalline, or hydrated acid ($ac' + q$) consists of

Anhydrous acetic acid	1	. . . 51	. . . 85	. . . Mollerat.
Water	1	. . . 9	. . . 15	. . . 87·125
<hr/>				
Crystallized acetic acid	1	60	100	100·000

It will be seen by referring to the atomic constitution of the *anhydrous acetic acid*, that it is represented by $(4\text{ car} + 3\text{ q})$, or $(4\text{ car} + 3\text{ h} + 3\text{ o})$, and that the *hydrated* or crystalline acid, represented by the formula $(4\text{ car} + 4\text{ q})$ or $(4\text{ car} + 4\text{ h} + 4\text{ o})$, may be regarded as including equal volumes of hydrogen and carbonic oxide.

CHARACTERS OF THE ACETATES.—It has already been stated that these salts are soluble in water; there are, perhaps, two exceptions, in those of molybdenum and of tungsten, and the acetate of silver and of protoxide of mercury are difficultly soluble. The acetates are decomposed by heat, and yield variable products; those of the alkaline bases yield carbonates, carbonic acid, oxide of carbon, a little carburetted hydrogen, a small quantity of water and of oil, and *pyroacetic spirit*, or *acetone*. Some of the acetates yield acetic acid scarcely altered; and some, a mixture of acid and spirit, leaving charcoal, and the metal or its oxide. The fusible acetates concrete, on cooling, into foliated masses. When acetates are in dilute aqueous solution, they often suffer spontaneous decomposition; some of them become carbonates, and a green mould forms upon their surface. These salts are recognised by the evolution of acetic acid when acted on by sulphuric acid; and many of them yield a precipitate of nacreous crystalline scales, with a solution of protonitrate of mercury.

ACETATE OF AMMONIA.—In solution, obtained by saturating distilled vinegar with carbonate of ammonia, it constitutes the *liquor ammoniæ acetatis* of the *Pharmacopœia*, which has long been used in medicine as a diaphoretic, under the name of *spirit of Mindererus*. When equal weights of acetate of potassa and sal-ammoniac are distilled together, ammonia is evolved, and binacetate of ammonia distils over in the form of an oily liquid which concretes into acicular crystals, deliquescent and soluble in alcohol. By passing dry ammonia into the fused binacetate it is converted into solid neutral acetate, which is a white inodorous salt, readily soluble in water and alcohol, and which is converted by heat into ammonia and binacetate. The formula of this salt is $(4\text{ car} + 3\text{ h} + 3\text{ o}) + (n + 3\text{ h}) + (\text{h} + \text{o})$, or $(4\text{ car} + 3\text{ h} + 3\text{ o}) + (n + 4\text{ h} + \text{o})$, that is, it is either hydrated acetate of ammonia, or anhydrous acetate of oxide of ammonium: its proportionals are

Ammonia	1	. . . 17	. . . 22·05
Acetic acid	1	. . . 51	. . . 66·25
Water	1	. . . 9	. . . 11·70
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Acetate of ammonia	1	77	100·00

ACETATE OF POTASSA ($\text{P} + \text{ac}'$) is usually formed by saturating distilled vinegar with carbonate of potassa, and evaporating to dryness. It is best obtained by saturating pure acetic acid, diluted with 2 or 3 parts of water, with the alkaline carbonate. If this salt be carefully fused, it

concretes into a lamellar deliquescent mass on cooling. It is the *terra foliata tartari*, and *febrifuge salt of Sylvius*, of old pharmacy. It dissolves in its own weight of water at 60° , and the solution has a pungent and sweetish saline taste. Boiling alcohol dissolves twice its weight. When chlorine is passed through the aqueous solution of this salt, carbonic acid is evolved, and a powerful bleaching-liquid formed; exposed to air, it gives out chlorine; distilled, it yields acetic acid, a little chlorine, and no oxygen. Carbonic acid decomposes the alcoholic solution of acetate of potassa, carbonate of potassa is deposited, and acetic acid, which produces some acetic ether, is set free. Acetate of potassa exists in the sap of several plants, which, when burned, yield carbonate of potassa*. In its anhydrous state this salt consists of

				Wenzel.	Richter.
Potassa	1	48	48.5	50.15	51.4
Acetic acid	1	51	51.5	49.85	48.6
Acetate of potassa	1	99	100.0	100.00	100.0

ACETATE OF SODA. ($S+ac'$).—This is an easily-crystallizable salt; its forms are very complex, and are derived from an oblique rhombic prism. (BROOKE, *Ann. of Phil.*, 2nd series, vi. 39.) When it contains a little tar, the crystals are often bulky; they effloresce in dry air, are soluble in 3 parts of cold and less of boiling water, and in 5 parts of alcohol. This salt has a saline, but not disagreeable flavour; it fuses when heated, and concretes into a lamellar mass, formerly called *terra foliata mineralis*. It is of importance, as above stated, as a source of acetic acid; at a red heat it leaves a mixture of carbonate of soda and carbon, in a favourable state for the preparation of sodium. The *anhydrous* salt consists of

				Berzelius.	Wenzel.
Soda	1	32	38.5	38.311	39.67
Acetic acid	1	51	61.5	61.689	60.33
Anhydrous acetate of soda	1	83	100.0	100.000	100.00

The crystallized salt ($S+ac'+6q$) includes 6 atoms of water, or

				Thomson and Berzelius.
Soda	1	32	23.4	22.94
Acetic acid	1	51	37.2	36.95
Water	6	54	39.4	40.11
Crystallized acetate of soda	1	137	100.0	100.00

* ALKARSINE. ($4car+6h+2ar+o$).—A compound represented by the preceding formula is obtained when equal weights of acetate of potassa and arsenious acid are slowly heated to redness in a glass retort placed in a sandheat and connected with a receiver surrounded by ice; carbonic acid and inflammable gases are disengaged, metallic arsenic sublimes, and two liquids pass over, the heavier of which is washed with water and rectified, first over caustic potassa, and then over lime. The alkarsine passes over

in the form of a colourless liquid boiling at 300° , and congealing at -10° . The density of its vapour is 7.8. Its odour is that of arsenuretted hydrogen, highly offensive and poisonous.

Alkarsine is sparingly soluble in water, but mixes in all proportions with alcohol and ether; it inflames spontaneously in the air. It has been the subject of an extended set of experiments by Bunsen and by Berzelius, of which an abstract will be found in LIEBIG's *Chimie Organique*.

ACETATE OF LITHIA is a very deliquescent and difficultly-crystallizable salt.

ACETATE OF LIME ($C + ac'$) forms silky acicular prisms of a bitterish saline taste, which effloresce when heated to 212° , and are soluble in water and alcohol; this salt is used in the formation of acetate of soda in the process for procuring acetic acid; heated to 226° , it is phosphorescent when triturated in the dark. It consists of

			Berzelius.	Higgins.	Richter.
Lime	1	28	35.4	35.7	34.3
Acetic acid	1	51	64.6	64.3	65.7
Acetate of lime	1	79	100.0	100.0	100.0

ACETATE OF BARYTA ($B + ac'$) is formed by digesting sulphuret of barium or carbonate of baryta in acetic acid, filtering and evaporating; dried at 212° , it yields a white powder, soluble in about its weight of water, sparingly soluble in alcohol, and of an acrid pungent taste: when crystallized at a temperature below 60° , it includes, according to Mitscherlich, 3 atoms of water, and its form resembles that of acetate of lead; above 60° it forms crystals with 1 atom of water, which are irregular six-sided prisms, terminated by dièdral summits, the primary form of which is a right rhomboidal prism. (BROOKE, *Ann. of Phil.*, 2nd series, vii. 365.) In cold weather the concentrated solution concretes into a congeries of silky crystals. It is sometimes used as a test of sulphuric acid. The *anhydrous* salt consists of

			Bucholz.	Richter.
Baryta	1	77	60.2	59.4
Acetic acid	1	51	39.8	40.6
Anhydrous acetate of baryta	1	128	100.0	100.0

and the common *crystallized* acetate contains:—

			Bucholz.
Baryta	1	77	56.2
Acetic acid	1	51	37.2
Water	1	9	6.6
Crystallized acetate of baryta	1	137	100.0

ACETATE OF STRONTIA ($STR + ac'$) is a very soluble salt, which, when crystallized, includes 2 atoms of water. The crystals formed below 60° contain 4 atoms of water.

ACETATE OF MAGNESIA ($M + ac'$) is a very difficultly crystallizable salt; it is generally obtained in the form of a gum-like mass, slightly deliquescent, soluble in water and alcohol, and composed of

			Richter.
Magnesia	1	20	28.9
Acetic acid	1	51	71.1
Acetate of magnesia	1	71	100.0

ACETATE OF MANGANESE. ($MAN + ac'$).—This salt is prepared for the use of calico-printers, by mixing sulphate of manganese with acetate of lime. It forms transparent pale-red rhomboidal tables, soluble in water and alcohol. When printed upon calico and passed through a

bath of chloride of lime, a brown oxide of manganese is formed upon the fibre.

PROTACETATE OF IRON. ($\text{Fe} + \text{ac}'$).—This salt is obtained by the action of acetic acid on protosulphuret of iron: it forms a mass of white silky crystals when evaporated out of contact of air. When iron filings are digested in acetic acid, the resulting solution contains a mixture of peracetate and protacetate. When acetate of baryta or acetate of lead, and protosulphate of iron, are mixed in atomic proportions, double decomposition ensues, and protacetate of iron and sulphate of baryta or of lead are the results.

PERACETATE OF IRON ($\text{fe} + 14\text{o} + 14\text{ac}'$) may be obtained by digesting turnings and clippings of iron in acetic acid; or by dissolving peroxide of iron in the acid; or by mixing acetate of lead or of baryta with persulphate of iron: it forms a deep reddish-brown solution, which, when carefully concentrated, yields a gelatinous residue, but does not crystallize; if rapidly evaporated, it deposits a yellow powder, which is said to be a diacetate. This solution is much employed by dyers and calico-printers.

ACETATE OF ZINC ($\text{Zn} + \text{ac}'$) is formed either by dissolving oxide of zinc in acetic acid, or by mixing a solution of sulphate of zinc with one of acetate of lead. It crystallizes in thin shining rhomboidal plates, of a bitter and metallic taste, very soluble, but not deliquescent: their primary form is an oblique rhombic prism. (BROOKE, *Ann. of Phil.*, 2nd series, vi. 39.) This salt is sometimes used in pharmacy, chiefly as an external application. According to Messrs. Aikin, the specific gravity of a saturated solution of acetate of zinc, made by digesting the metal in distilled vinegar, is 1.055. Of this solution, 900 grains contain 53 of dry, or 82.6 of crystallized acetate. One ounce, by measure, of the solution, weighs 506 grains, and contains 29.8 grains of dry, or 46.5 grains of crystallized salt. This salt, in its usual crystallized form, includes, according to Thomson, 7 atoms of water, but it also crystallizes with 3 atoms.

ACETATE OF TIN.—This metal is slowly acted on by acetic acid, but a *protacetate* and *peracetate of tin* may be made by mixing acetate of lead with saturated solutions of the protochloride and perchloride of tin. These solutions have been recommended as mordants for the use of dyers. The protacetate is crystallizable. Vinegar, kept in tin vessels, dissolves a very minute portion of the metal; and in pewter vessels, it likewise dissolves a small portion of the lead, where in contact both with the vinegar and air; hence, distilled vinegar, which has been condensed in a pewter worm, affords generally traces of both metals. (VAUQUELIN, *Ann. de Ch.*, xxxii.)

ACETATE OF CADMIUM. ($\text{Cad} + \text{ac}' + 2\text{q}$).—When a concentrated solution of this salt is exposed for about ten days to the air, it is gradually converted into a crystalline mass, while a dense liquid remains above it. The crystals are prisms, very soluble in water, and not altered by exposure to air: they include 2 atoms of water. (THOMSON.)

ACETATE OF COBALT.—Oxide of cobalt is easily soluble in acetic acid, forming a red solution; it yields a red deliquescent salt when carefully evaporated, becoming blue when heated, and forming a good sympathetic ink. (ILSEMANN, *Crell's Annals*, 1785, ii. 25.)

ACETATE OF NICKEL. ($\text{NiC} + \text{ac}' + 5 \text{q.}$)—Carbonate of nickel dissolves readily in acetic acid, forming a dark green solution, from which rhomboidal crystals may be obtained, soluble in water, but insoluble in alcohol; when heated, they give out water and become yellow, then burn like tinder, and leave oxide of nickel: they include 5 atoms of water. (THOMSON.)

ACETATE OF COPPER. ($\text{Cu} + \text{ac}' + \text{q.}$)—This salt is generally distinguished as *crystallized verdigris*: it has been long known, and is described by Pliny (lib. xxxiv., c. ii.) It is prepared by dissolving the *subacetate* or *common verdigris* in acetic acid; the solution is put into pans and allowed slowly to crystallize, generally upon twigs or pieces of string suspended in it: it forms oblique rhombic prisms (BROOKE, *Ann. of Phil.*, 2nd series, vi. 39), of a rich blueish-green colour, soluble in 5 parts of boiling water, and sparingly soluble in alcohol. The dilute aqueous solution is decomposed when boiled, and deposits a tribasic salt. When this salt is heated in the air, it burns with a green flame; submitted to destructive distillation, it yields water, acetic acid, pyroacetic spirit, carburetted gases, and a white crystalline sublimate, which is an *acetate of the suboxide of copper*; it leaves a residue of very finely-divided copper mixed with a little charcoal, which burns like tinder when heated, and at a high temperature is pyrophoric. This salt was formerly a principal source of strong acetic acid, but since the discovery of the modes of purifying and concentrating pyroligneous acid, it has fallen into disuse. When sugar is added to a boiling solution of acetate of copper, a red crystalline powder, said to be pure suboxide of copper, falls, and the remaining filtered solution contains some peculiar combination of copper, which has not, I believe, been accurately examined. This salt, when crystallized at temperatures below 50° , sometimes forms oblique 4-sided prisms, which include 5 atoms of water, and which when heated to 86° crack into small crystals of the ordinary monohydrated salt, giving off 4 atoms of water. The salt, as it usually occurs, consists of

			Phillips.	Ure.	Gehlen.	Berzelius.
Oxide of copper	1	40	39.2	39.6	40	39.29
Acetic acid	1	51	49.9	52.0	60	60.71
Water.	1	9	10.9	8.4		
Crystallized acetate of copper	1	100	100.0	100.0	100	100.00

DIACETATE OF COPPER. **SUBACETATE OF COPPER.** ($2\text{Cu} + \text{ac}' + 6 \text{q.}$)—This dibasic salt is the common *verdigris* or *ærugeo* of commerce; it is prepared by exposing thin plates of copper to the action of acetic acid, or its fumes; the method now practised consists in alternating plates of copper with pieces of woollen cloth steeped in acetic acid; they gradually become corroded and superficially covered with verdigris, which is from time to time removed, and the operation repeated as long as the plate lasts. Sometimes the husks and stalks of grapes or raisins, in a state of

acetous fermentation, are employed to act upon the copper, as is the case with some of the French verdigris. This article is commonly rolled or packed in white leather, and is frequently much adulterated with a mixture of chalk and sulphate of copper. Pure diacetate of copper is in small silky crystals; when moistened a little it crumbles, and is only partially soluble in water. This salt consists of

Oxide of copper	2	80	43·24	Berzelius. 43·34
Acetic acid	1	51	27·57	27·45
Water	6	54	29·19	29·21
Hydrated diacetate of copper	1	185	100·00	100·00

Mr. Phillips has given the following comparative statement of the composition of the different kinds of verdigris. (*Ann. of Phil.*, second series, vi. 39.)

	Blue Crystals.	French Verdigris.	English Verdigris.
Acetic acid	28·30	29·3	29·62
Peroxide of copper	43·25	43·5	42·25
Water	28·45	25·2	27·51
Impurity	0	2·0	0·62
	100·00	100·0	100·00

SUBSESQUIACETATE OF COPPER. ($1\frac{1}{2}\text{Cu} + \text{ac}' + 3\text{q.}$)—This sesqui-basic salt is obtained by triturating the diacetate with water, filtering the solution, concentrating it by slow evaporation, heating so as to dissolve the deposit, and then adding alcohol; when the solution is set aside, a gelatinous mass of minute crystals is formed, which when dry are of a pale blue colour, and consist of

Oxide of copper	$1\frac{1}{2}$	60	43·48	Berzelius. 43·19
Acetic acid	1	51	36·96	36·80
Water	3	27	19·56	20·01
Hydrated subsesquiacetate of copper	1	138	100·00	100·00

TRISACETATE OF COPPER. ($3\text{Cu} + \text{ac}' + 2\text{q.}$)—This tribasic salt is the portion of the *diacetate* which is insoluble in water, and which, when thoroughly washed with alcohol, and dried at 212° , consists of

Oxide of copper	3	120	63·5	Berzelius. 64·36
Acetic acid	1	51	27·0	27·60
Water	2	18	9·5	8·04
Hydrated trisacetate of copper	1	189	100·0	100·00

ACETATE OF LEAD. ($\text{Pl} + \text{ac}' + 3\text{q.}$)—The oxide of lead combines, like the oxide of copper, in several proportions with acetic acid. The *neutral acetate* has long been known under the name of *sugar of lead*; it is the *salt of Saturn* of the old chemists, and is a considerable article of commerce, being much used in various operations connected with dyeing and calico-printing. It is prepared by digesting oxide of lead in pyroligneous acid, or in pure acetic acid, and is found, in trade, of various degrees of purity, according to the purposes for which it is intended. When plates of lead are exposed to the fumes of vinegar or acetic acid, they become corroded and incrustated with a mixture of acetate and car-

bonate of lead, and which, scraped off and dissolved in excess of acetic acid, forms a solution from which crystallized acetate of lead is obtained by evaporation. Litharge, or other oxides of lead, may also be used in this process. This salt crystallizes in acicular masses, when its hot concentrated solution is set aside to cool, and in this state it is generally found in commerce; by slower evaporation, it yields truncated and flattened quadrangular and hexaëdral prisms, cleavable parallel to the lateral and terminal planes of a right rhombic prism, which may be considered as its primary form. (BROOKE, *Ann. of Phil.*, 2nd series, vi. 374.) These crystals are permanent in ordinary states of the atmosphere, but they effloresce and become anhydrous at about 100° , *in vacuo* over sulphuric acid; they also gradually become anhydrous, at a temperature between 70° and 80° . The anhydrous acetate is soluble in boiling absolute alcohol, and on slow cooling is deposited in hexagonal tables. Acetate of lead has a singularly sweet, and somewhat astringent, taste: its sp. gr. is 2.57. Water boiled upon it dissolves 0.29, and retains, when cold, 0.27 of its weight of it. (BOSROCK.) According to Payen (*Ann. de Ch. et Ph.*, LXvi. 42) 100 parts of water at 60° dissolve 59 of the crystals. It does not raise the boiling-point of water. It dissolves in 8 parts of alcohol. When heated, the crystals fuse at about 130° ; at 212° the liquid salt boils, and having lost its water of crystallization, concretes into a lamellar mass; at a higher temperature, this fuses, then gives out acetic acid, acetone, and carbonic acid, and the residue of its destructive distillation is charcoal, and very finely-divided lead, in a highly combustible or pyrophoric state. A brown or impure sugar of lead, made by digesting litharge in rough pyroligneous acid, is manufactured expressly for the use of dyers.

Acetate of lead is partially decomposed by carbonic acid, which throws down a portion of carbonate of lead, and the acetic acid which is set free protects the remaining solution from further precipitation; the carbonic acid contained in the atmosphere partially decomposes acetate of lead in this way. All the acids and their salts, which form insoluble or difficultly soluble compounds with oxide of lead, also decompose this salt, and these are very numerous; and in consequence of the facility with which the insoluble salts of lead are decomposed, when diffused through water, by sulphuretted hydrogen, such applications of the acetate are of frequent occurrence. The fixed alkalis throw down hydrated oxide of lead from the solution of the acetate, but pure ammonia does not at first precipitate the cold aqueous solution, but forms a precipitate of oxide of lead when boiled. The crystallized acetate consists of

				Berzelius.	Thenard.
Oxide of lead	1	112	58.95	58.71	58
Acetic acid.	1	51	26.84	26.97	26
Water	3	27	14.21	14.32	16
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Crystallized acetate of lead	1	190	100.00	100.00	100

SESQUIBASIC ACETATE OF LEAD. ($1\frac{1}{2}\text{Pb} + \text{Ac}$).—This salt is obtained in the form of pearly six-sided scales, soluble in water and alcohol, by fusing the neutral acetate till it forms a white spongy mass, the solution of which is evaporated to the consistence of syrup and set aside to crystallize.

DIACETATE OF LEAD. ($2\text{Pl} + \text{ac}' + 10\text{q.}$)—This salt is formed, according to Thomson, by boiling a solution of acetate of lead with the requisite atomic proportion of litharge: on evaporation, it falls as a white crystalline sediment, of a sweet astringent taste, and soluble in water. Its constituents are

				Thomson.
Oxide of lead	2	224	61.2	
Acetic acid	1	51	14.0	
Water	10	90	24.8	
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Hydrated diacetate of lead	1	365	100.0	

TRISACETATE OF LEAD. ($3\text{Pl} + \text{ac}'$).—This tribasic acetate has long been known, in solution, under the name of *Goulard's Extract of Lead*. It is the *Liquor plumbi subacetatis* of the Pharmacopœia. It is prepared by boiling excess of finely powdered protoxide of lead in a solution of the acetate, or in dilute acetic acid. About 15 parts of litharge to 10 of the crystallized acetate may be used; about 6 parts are dissolved; and the solution, filtered and evaporated, leaves an anhydrous *trisacetate*. According to Payen a tribasic acetate of lead is also thrown down, when slight excess of ammonia is added, drop by drop, to a cold solution of acetate of lead. This salt is soluble in water; at 212° 100 parts of water dissolve 18 parts of the salt, and the saturated solution yields silky crystals on cooling; it is insoluble in absolute alcohol. It has an alkaline reaction. It is a very susceptible test of the presence of carbonic acid, which it absorbs from the atmosphere, and suffers a proportionate decomposition; even distilled water is seldom so free from carbonic acid as not to be rendered turbid on the addition of a few drops of the solution of this salt. It forms precipitates in all solutions which affect the neutral acetate, and it throws down the greater number of organic compounds, hence its use in many cases of analysis. The anhydrous salt consists of

				Berzelius.
Oxide of lead	3	336	86.82	86.77
Acetic acid	1	51	13.18	13.23
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Trisacetate of lead	1	387	100.00	100.00

HEXACETATE OF LEAD. ($6\text{Pl} + \text{ac}'$).—When 1 part of acetate of lead and 2 of litharge are boiled together, or when acetate of lead is decomposed by excess of ammonia, a white powder is obtained, of very sparing solubility, and consisting of

				Berzelius.
Oxide of lead	6	672	89.60	91.3
Acetic acid	1	51	6.80	5.7
Water	3	27	3.60	3.0
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Hydrated hexacetate of lead	1	750	100.00	100.0

ACETATE OF ANTIMONY.—This salt, formed by digesting the protoxide in vinegar, was once employed as an emetic.

ACETATE OF BISMUTH may be formed by adding nitrate of bismuth to a concentrated solution of acetate of potassa; a precipitate falls, which redissolves on the application of heat, and afterwards affords scaly

crystals. The addition of acetic acid to nitrate of bismuth prevents its precipitation when diluted. (MORVEAU, *Ency. Method.*, CHIMIE.)

ACETATE OF URANIUM forms four-sided prismatic crystals of a yellow colour.

ACETATE OF CERIUM.—Recently-precipitated oxide of cerium readily dissolves in acetic acid, and yields small crystals on evaporation, of a sweetish taste, permanent, and readily soluble in water. (HISINGER and BERZELIUS; *Gehlen's Jour.*, ii. 414.)

PROTACETATE OF MERCURY ($\text{Hg} + \text{ac}'$) is most readily formed by mixing a solution of protonitrate of mercury with acetate of potassa. For this purpose dissolve 3 ounces of mercury in about $4\frac{1}{2}$ ounces of cold nitric acid, and mix this solution with 3 ounces of acetate of potassa previously dissolved in 8 pints of boiling water, and set the whole aside to crystallize, which takes place as the liquor cools, and the acetate of mercury then separates in the form of micaceous crystalline plates, which are to be washed in cold water, and dried on blotting-paper. (*Edin. Phar.*) In preparing this salt, the quantity of water for dissolving the acetate need not be so large as above directed, 1 pint being sufficient, but it is necessary to pour the mercurial solution into the acetate. This salt has an acrid taste, and is very difficultly soluble in water, requiring, according to Braconnot (*Ann. de Ch.*, LXXXVI. 92), 600 parts of water. It is insoluble in alcohol. It should be dried in the dark, as light has a tendency to decompose it. It was once used in medicine, especially as an ingredient in *Keyser's Pills*. It consists of

				Dumas.	Garot.
Protoxide of mercury .	1	208	80.3	80.66	79.7
Acetic acid	1	51	19.7	19.34	20.3
Protacetate of mercury	1	259	100.0	100.00	100.0

PERACETATE OF MERCURY ($\text{hg} + 2\text{o} + \text{ac}'$) is obtained by boiling peroxide of mercury in acetic acid; on cooling, nacreous crystals are deposited, readily soluble in water, and composed of

				Stromeyer.	Garot.
Peroxide of mercury .	1	216	67.9	67.664	67.
Acetic acid	2	102	32.1	32.336	33.
Peracetate of mercury	1	318	100.0	100.000	100.

ACETATE OF SILVER. ($\text{Ag} + \text{ac}'$).—This is a very difficultly soluble salt, and much resembles the protacetate of mercury. It is deposited in lamellar crystals when acetic acid is added to a strong solution of nitrate of silver; it is abundantly precipitated from a mixed solution of nitrate of silver and acetate of soda. Its difficult solubility renders nitrate of silver useful occasionally as a test of acetic acid. It consists of

				Dumas.
Oxide of silver .	1	116	69.46	70.33
Acetic acid	1	51	30.54	29.67
Acetate of silver	1	167	100.00	100.00

ACETATE OF ALUMINA.—This salt is extensively employed by dyers and calico-printers as a basis or mordant for fixing a great variety of

colours: it is usually made by mixing solutions of alum and acetate of baryta or of lead. About 3 lbs. of alum are generally dissolved in 8 gallons of water, and a pound and a half of sugar of lead stirred into it; a copious formation of sulphate of lead ensues, which is allowed to subside, and the clear liquor holding acetate of alumina, and a portion of undecomposed alum in solution, is then drawn off; a portion of pearlash and chalk being added to it previous to use, in order to saturate any excess of acid. This salt is also produced by the mutual decomposition of acetate of lime and alum. A gallon of a solution of acetate of lime, of a specific gravity of about 1.050, equivalent to nearly half a pound avoirdupois of dry acetic acid, is employed for every $2\frac{3}{4}$ lbs of alum. (URE'S *Dictionary*, Art. ALUMINA.)

Acetate of alumina, formed by digesting recently-precipitated alumina in acetic acid, may be procured in deliquescent acicular crystals of an astringent taste, and containing, according to Richter, 73.81 acid + 26.19 alumina: hence it is probably a *binacetate*.

The solution of this salt becomes turbid when heated, and again transparent on cooling; a curious circumstance, first observed by Gay Lussac, and depending upon a temporary decomposition of the acetate; whether the deposit be alumina or a subacetate seems not understood; it is prevented in the solutions used by the calico-printer, by excess of alum.

ACETONE. PYROACETIC SPIRIT. PYROACETIC ETHER.—This product was obtained by Derosne, along with acetic acid, by the destructive distillation of acetate of copper. (*Ann. de Chim.*, LXiii. 267.) Chenevix obtained it from other acetates, and it has subsequently been examined by Macaire and Marcet (*Ann. of Phil.*, N. S., viii. 69), and by Liebig and Dumas. (*Ann. de Ch. et Ph.*, xlix.) When acetate of lime is carefully distilled, it yields a considerable portion of this product; it may be freed from water and empyreumatic oil, by repeated rectification over chloride of calcium. It is, when pure, a colourless limpid liquid, highly inflammable, of a peculiar penetrating and somewhat aromatic odour; specific gravity = 0.792 at 64°. It boils at 132°, and the density of its vapour is, according to Dumas, 2.019. It mixes in all proportions with water, alcohol, ether, and oil of turpentine; it is not affected by exposure to air; it may be distilled without change over the caustic alkalis and chloride of calcium; but when mixed with fixed alkaline solutions, and exposed to air, oxygen is absorbed, and a brown matter slowly formed. It dissolves saline substances generally, less copiously than alcohol. Distilled with chloride of lime it yields *chloroform*. Gaseous chlorine is absorbed by it, with the evolution of hydrochloric acid and the formation of a peculiar oily fluid of the specific gravity 1.33, and composed of ($3\text{car} + 2\text{h} + \text{c} + \text{o}$). (LIEBIG.) The action of acetone on deutochloride of platinum has been studied by Zeise. (*Ann. de Ch. et Ph.*, LXXii. 113.)

The ultimate components of acetone appear to be

				Dumas.	Macaire and Marcet.
Carbon	3	18	62.1	62.5	55.30
Hydrogen	3	3	10.3	10.2	8.20
Oxygen	1	3	27.6	27.3	36.50
Acetone	1	29	100.0	100.0	100.00

The product analyzed by Macaire and Marcet was probably not pure. Liebig and Dumas have observed that *anhydrous acetate of baryta* is resolved by heat into pyroacetic spirit and carbonate of baryta, and it will be found that

1 equivalent of acetic acid = 51, or ($4\text{ car} + 3\text{ h} + 3\text{ o}$)
may be exactly resolved into

1 equivalent of pyroacetic spirit = 29, or ($3\text{ car} + 3\text{ h} + \text{o}$)
1 ————— carbonic acid = 22, or ($\text{car} + 2\text{ o}$)

METACETONE.—Fremy has given this name to a product obtained by distilling a mixture of 1 part of sugar with 8 of quicklime: it is a colourless liquid, insoluble in water, but soluble in alcohol and ether: it has an agreeable odour, and boils at 183° . (*Ann. de Ch. et Ph.*, lix. 5.) It consists of

				Fremy.
Carbon . .	6 . .	36 . .	73.47 . .	72.37
Hydrogen .	5 . .	5 . .	10.20 . .	10.15
Oxygen . .	1 . .	8 . .	16.33 . .	17.48
Metacetone	1	49	100.00	100.00

PYROXYLIC SPIRIT. PYROLIGNEOUS SPIRIT. BIHYDRATE OF METHYLENE. (From $\mu\epsilon\theta\nu$, *wine*, and $\upsilon\lambda\eta$, *wood*.)—We owe the discovery of this product to Mr. Philip Taylor (*Quart. Jour. of Science*, xiv. 436); it was afterwards examined by Macaire and Marcet (*Bibl. Univ. and Ann. of Phil.*, N.S., viii. 62), then by Döberiner, by Colin, and by Liebig, by Dumas and Peligot, (*DUMAS, Chim. app. aux Arts*, v. 419,) and by Mr. Kane of Dublin. (*Ann. der Pharm.*, xix. 164.) When wood is subjected to destructive distillation there is formed, along with the tar, acetic acid, and other products already described, a variable portion, amounting on an average to about 1 per cent., of a highly inflammable and volatile liquid; it may be separated, to a certain extent, from the water and acetic acid, by distillation and separation of the first products; and these, redistilled and rectified over quicklime, at length afford the pure *pyroxylic spirit*, or *alcohol of wood*. If it contain ammonia, it must be neutralized, previous to its last rectification, by sulphuric acid*. Mr. Kane purifies the spirit by saturating it with dry chloride of calcium; the saturated solution furnishes

* The experiments which have been made upon pyroxylic spirit, show its close connexion with alcohol, and lead us to suspect that, at no very remote period, *alcohol* will rank among the other extraordinary products which are derived from *lignin*. Although this *spirit* has not, I believe, as yet been rendered palatable, or resorted to as a stimulant, it is much used as a substitute for alcohol in the manufacture of varnishes and other purposes of the arts. The varnish with which hats are rendered waterproof is made by dissolving shell-lac in pyroligneous spirit. It is also commonly employed (often under the name of *naphtha*) to burn in lamps, as a cheap substitute for spirit of wine. The chemical characters of *pyroxylic spirit*, as opposed to those of *alcohol*, are apparently sufficient, when carefully observed, to enable us satisfactorily to distinguish them; but articles are imported under the name of *pyroligneous ether, spirit, &c.*, which are most suspiciously identical with alcohol, and which, if not closely examined, may lead to serious frauds upon the revenue: strong alcohol, so disguised as to smell and taste as in those respects to resemble pyroxylic spirit, has already been found in the market.

hexagonal tabular crystals, which he distils over a water-bath as long as they yield spirit, and then, adding water, continues the distillation.

Pyroxylic Spirit is a limpid liquid, of a peculiar odour, partaking of that of alcohol and acetic ether, with an aromatic taint which has been compared to peppermint. Its taste is hot and pungent. Its specific gravity at 60° is about 0.800. It boils at 150° (151.7 under a pressure of 29.96 in mercury); if heated in a retort, even in a water-bath, the sudden extrications of its vapour are troublesome, and may be prevented by the presence of a little mercury, which equalizes the distribution of heat. The density of its vapour is 1.115 (1.120 at 212°). It is not altered by exposure to air, but when subjected to the slow action of black platinum it yields *formic acid*; not acetic acid, as is the case with alcohol. When pure it is not discoloured by the action of air and light, mixes in all proportions with water without becoming turbid, does not form a black precipitate with protonitrate of mercury, and has no action on vegetable test papers.

Chlorine acts less powerfully on pyroxylic spirit than on alcohol, and heat is required to accelerate their mutual action; it gives rise to the production of two liquids of very different degrees of volatility; that which is least volatile forms a crystallizable compound with ammonia. Chloride of lime acts upon pyroxylic spirit as it does upon alcohol; it also dissolves potassa and soda with similar phenomena. It dissolves baryta with the evolution of heat; and with solution of potassa and sulphuret of carbon, it forms a product which resembles Zeise's hydroxanthate of potassa. Its solvent powers, in regard to *salts*, closely resemble those of alcohol, and it has been stated that it may be substituted for alcohol in the preparation of fulminating silver, though the action is less violent and the product smaller in quantity; but, according to Dumas and Peligot, the product is *oxalate*, and not fulminate of silver; so also it converts nitrate into oxalate of mercury. It dissolves the resins, and may be used as an excellent substitute for alcohol in all varnishes; indeed, its superior volatility renders it preferable.

PROTOHYDRATE OF METHYLENE.—When 1 part of pyroligneous spirit is distilled with 4 of sulphuric acid, abundance of gas is evolved; when this is collected over mercury, it is found to consist of carbonic and sulphurous acids, which may be abstracted by potassa, and of *Hydrate of methylene*, a gaseous body, having a specific gravity = 1.61, and composed of

		Sp. Gr.
1	volume carbon vapour	0.8432
2	„ hydrogen gas	0.1376
1	„ aqueous vapour	0.6200

1.6008 (DUMAS.)

This gas, therefore, according to Dumas, is isomeric with alcohol, and the vast difference in their respective properties depends upon the different densities of their hydrocarbon; the hydrogen and carbon which constitute 1 volume of alcoholic hydrocarbon, forming 2 volumes of methylic hydrocarbon.

The gas is colourless, of an ethereal odour, and burns with a flame

resembling that of alcohol; water dissolves about 37 times its volume of it, at 65° , and acquires an ethereal odour and pungent taste: it is more soluble in alcohol and in pyroxylic spirit; it also dissolves in sulphuric acid, and is again evolved when water is added. It is presumed to consist of 1 atom of methylene and 1 of water.

COMBINATIONS OF METHYLENE WITH THE HYDRACIDS.—The hydracids act upon pyroxylic spirit, producing compounds analogous to the ethers of those acids, the water of the pyroxylic spirit being thrown off, and replaced by the acid, in such a way that each volume of the new compound includes 1 volume of methylene and 1 volume of the acid; these compounds are neutral, and show no indications of their included acids to tests, till the combination is destroyed by a red heat or by inflammation.

HYDROCHLORATE OF METHYLENE.—This compound is best obtained by heating a mixture of 2 parts of chloride of sodium, 1 of pyroxylic spirit, and 3 of sulphuric acid; a gas is evolved, which may be received over water, and which is pure hydrochlorate of methylene, any impurities being abstracted by the water. This gas is not condensable at 0° , it is colourless, of an ethereal odour, and sweet taste, and burns with a greenish white flame. Water at 60° , dissolves 2.8 volumes. It is quite neutral, and gives no precipitate with solution of nitrate of silver, resembling in these respects hydrochloric ether. Its density, determined by experiment, is 1.736, and analysis shows that it contains 1 volume of methylene. As the density of hydrochloric acid gas is = 1.2474, it is obvious that this ether is composed of 1 volume of methylene, and 1 volume of hydrochloric acid gas, condensed into 1 volume, for

	1 volume of methylene	Sp. Gr.
	1 " hydrochloric acid gas . . .	0.4904
	1 " hydrochlorate of methylene	1.7378

COMBINATIONS OF METHYLENE WITH THE OXYACIDS.—The action of the oxyacids upon pyroigneous spirit, gives rise to two classes of products; the one corresponding to the compound ethers formed by alcohol; the other analogous to the sulphovinic or phosphovinic acids. The first are neutral, and contain 1 atom of methylene, 1 atom of acid, and 2 atoms of water; they are more volatile and more stable than the corresponding alcoholic compounds.

SULPHATE OF METHYLENE is produced in the form of a heavy oil-like liquid, during the distillation of 1 part of pyroxylic spirit with 8 or 10 of sulphuric acid; when the oil is purified, it has an alliaceous odour; its specific gravity is 1.324; when anhydrous it admits of redistillation without decomposition; cold water slowly decomposes it, but boiling water instantaneously, resolving it into regenerated pyroxylic spirit, and into *sulphomethylic acid*; it is also decomposed by the hydrated alkalis.

The composition of this oil is stated by Dumas to be 22.5 methylene, 63.3 sulphuric acid, 14.2 water.

In regard to the other combinations of methylene, I must refer to the authorities quoted, or to Dumas (*Chim. app. aux Arts*, v.)

According to Dumas and Peligot, *pyroxylic spirit* is composed of

					Dumas.	
Carbon	2	12	37.5	37.97		
Hydrogen	4	4	12.5	12.40		
Oxygen	2	16	50.0	49.63		
Pyroxylic spirit	1	32	100.0	100.00		

These numbers are equivalent to

Olefiant gas	1	14	43.8	
Water	2	18	56.2	
Pyroxylic spirit	1	32	100.0	

But the term *methylene* is applied, not to olefiant gas, but to a *hydrocarbon*, of which 1 volume contains 1 atom of carbon and 1 of hydrogen, so that its density is just half that of olefiant gas, being, according to Dumas, 0.4904; and in representing it by the equivalent 14, it is assumed that its atom corresponds to two volumes: if its equivalent be called 7, it will then correspond with its density, in reference to hydrogen as = 1, and in that case, pyroxylic spirit will be represented by

					Vols.	Sp. Gr.
Methylene	1	7	43.8	1	0.490	
Water	1	9	56.2	1	0.625	
Pyroxylic spirit	1	16	100.0	1	1.115	

And the *gaseous hydrate of methylene*, called above, the *protohydrate*, will consist of

					Vols.	Sp. Gr.
Methylene	2	14	60.9	2	0.980	
Water	1	9	39.1	1	0.625	
Dihydrate of methylene	1	23	100.0	1	1.605	

The *hydrochlorate of methylene*, in reference to this view, will then consist of

					Vols.	Sp. Gr.
Methylene	2	14	27.5	2	0.980	
Hydrochloric acid	1	37	72.5	2	2.494	
Hydrochlorate of methylene	1	51	100.0	2	1.737	

Hydrofluatate of Methylene was obtained by Dumas and Peligot (*Ann. de Ch. et Ph.*, Lxi. 193), by gently heating a mixture of fluoride of potassium and sulphate of methylene in a glass retort; it is gaseous, and is purified by collecting it over water. It is colourless, has an ethereal odour, burns with a blue flame, and develops hydrofluoric acid during its combustion. 100 parts of water at 60° absorb 166 parts (volumes). It is composed of

					Vols.	Sp. Gr.
Methylene	2	14	43.7	2	0.980	
Hydrofluoric acid	1	19	56.3	2	1.356	
Hydrofluatate of methylene	1	33	100.0	2	1.168	

The nature of *methylene* or the base of pyroxylic spirit requires further examination, but if the preceding views be correct, it furnishes the compound of 1 atom of carbon and 1 of hydrogen, which was required to

complete the series of hydrocarbons: its formula is (*car* + *h*) and its equivalent 7, and in reference to the diagrams which I have elsewhere employed, it may be represented as in the margin.

Hydrogen. 1	Carbon. 6	=	Methylene. 7
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It is impossible to review the facts which have been adduced respecting the atomic constitution of the various hydrocarbons, and their relations to oxygen and other substances, in the character of *bases*, without favourable anticipations in regard to the ultimate influence of these inquiries, in simplifying our views of organic compounds. Some of the theoretical inferences bearing upon this subject have perhaps been carried too far, and others are purely hypothetical, but it is only by thus viewing the question in different lights, and by associating and comparing the experimental results, that the problem respecting the atomic constitution of organic compounds can be ultimately solved; it will then, no doubt, be found that the complexity and incongruities which hang over the subject are *apparent* only, and that the fundamental doctrines of organic chemistry will admit of some simple enunciation.

TARTROMETHYLIC ACID.—The action of the tartaric and of the paratartaric acids on pyroligneous spirit has been examined by Guérin-Varry. (*Ann. de Ch. et Ph.*, Lxii. 77.) The products are analogous to the tartrovinic and paratartrovinic acids.

ALDEHYD. ($4\text{ car} + 4\text{ h} + 2\text{ o}$) or ($4\text{ car} + 3\text{ h} + \text{o}$) + *q*.—Among the results of the decomposition of ether and alcohol, a product has been adverted to under the name of *aldehyd* (*alcohol dehydrogenatus*). It was first noticed by Döbereiner, and examined by Liebig. (*Ann. de Ch. et Ph.*, Lix. 289.) Pure aldehyd is obtained by dissolving 2 parts of aldehyd-ammonia in water, and adding a cold diluted acid, composed of 3 parts of sulphuric acid and 4 of water; the mixture is distilled from a water-bath into a receiver surrounded by ice, and the product twice rectified with its bulk of chloride of calcium, at a temperature between 77° and 86°; it is then pure aldehyd.

Aldehyd is a colourless clear liquid, feebly refracting light, and of an ethereal suffocating smell: it mixes with water, alcohol, and ether, is neutral to test paper, and burns with a pale flame: it absorbs oxygen, and is converted into hydrated acetic acid; it dissolves iodine, sulphur, and phosphorus; solution of chlorine converts it into acetic acid. Sulphuric acid blackens it. With solution of potassa it yields a brown mixture, upon the surface of which a resin soon separates. When a solution of aldehyd is mixed with oxide of silver, the metal is reduced without evolution of gas, and a solution of aldehydate of silver is formed. When ammonia is added to a liquid containing aldehyd, and then nitrate of silver till all alkaline reaction ceases, the metal is also reduced. By long keeping, aldehyd spontaneously changes into two isomeric compounds, *metlaldehyd*, and *elaldehyd*; the former solid, the latter liquid.

ALDEHYD-AMMONIA. ($4\text{ car} + 3\text{ h} + \text{o}$) + ($n + 3\text{ h}$) + ($\text{h} + \text{o}$).—Liebig gives the following directions for the preparation of this compound:—

6 parts of sulphuric acid, 4 of water, 4 of alcohol, and 6 of binoxide of manganese, are distilled by a gentle heat into a tightly-fitted receiver cooled by ice: when the effervescence in the retort subsides, the product, which amounts to 6 parts, is removed and rectified with its weight of chloride of calcium; it now amounts to 3 parts, and is again rectified with the chloride of calcium, when 1.5 parts of a liquid are obtained, which is aldehyd mixed with a little water, alcohol, and acetic and formic ethers; this is mixed with its bulk of ether and saturated by dry ammonia, when crystals of aldehyd-ammonia separate, which are to be washed with ether and dried at common temperature.

Aldehyd-ammonia forms acute rhombic prisms, which are colourless, transparent, and strongly refract light: they have the mixed odour of ammonia and turpentine: they are volatile and fusible between 158° and 176° ; the vapour has an alkaline reaction: they distil unchanged at 212° , and become brown and acquire a burned odour by exposure to air; they dissolve in water and alcohol, but not in ether. Their concentrated solution gives a precipitate with nitrate of silver, which contains nitric acid, oxide of silver, ammonia, and aldehyd. When potassium acts upon aldehyd, heat and hydrogen are evolved, and a compound results which contains potassa, and reduces the salts of silver when aided by heat.

ALDEHYDIC ACID. ACETULOUS ACID. LAMPIC ACID. ($4\text{ car} + 3\text{ h} + 2\text{ o}$) + q , formed by heating oxide of silver in aldehyd; a soluble aldehydate of oxide of silver is produced, which may be decomposed by sulphuretted hydrogen, sulphuret of silver is thrown down, and a dilute solution of aldehydic acid remains; it may be neutralized by the alkalis, but on evaporation the aldehydic acid becomes converted into acetic acid and a resinous matter. Evaporated in vacuo it becomes yellow. Aldehydic acid is probably contained in Daniell's lampic acid (p. 1279, note).

ACETULE.—This term has been applied by Liebig to the hypothetical base or radical of aldehyd and of acetic acid: it is represented by the formula ($4\text{ car} + 3\text{ h}$). The anhydrous oxide of this radical is unknown, but aldehyd, aldehydic acid, and acetic acid, are assumed as hydrated oxides of such a radical; and etherine may, in accordance with certain hypothetical views of its compounds, be considered as a hydruret of the same radical, or as represented by the formula ($4\text{ car} + 3\text{ h}$) + h . The following are the comparative formulæ of these compounds:—

Acetule	($4\text{ car} + 3\text{ h}$)
Oxide of acetule	($4\text{ car} + 3\text{ h}$) + o
Aldehyd	($4\text{ car} + 3\text{ h} + o$) + ($h + o$)
Aldehydic acid	($4\text{ car} + 3\text{ h} + 2\text{ o}$) + ($h + o$)
Acetic acid	($4\text{ car} + 3\text{ h} + 3\text{ o}$) + ($h + o$)
Etherine	($4\text{ car} + 3\text{ h}$) + h
Ethule	($4\text{ car} + 3\text{ h}$) + 2 h

CHAPTER VIII.

ANIMAL PRODUCTS.

THE principal ultimate elements of animal substances are the same as those of vegetables, namely, carbon, hydrogen, oxygen, and nitrogen; but nitrogen is more generally present, and sulphur and phosphorus are more commonly superadded. The humidity of the proximate components, their organization, and their ultimate composition, are such, as in many cases to render them extremely prone to change, after the loss of vitality; and the very circumstances which contribute to their permanence and stability whilst under the influence of life, are, apparently, those which after death render them particularly susceptible of decomposition. The putrefaction of animal substances is distinguished from that of most vegetables by the nauseous stench which attends it, partly arising from the presence of sulphur and phosphorus in the gaseous products, and partly from other combinations, with the exact chemical nature of which we are unacquainted.

The *solids of animals* derive their soft, flexible, or elastic texture, partly from their peculiar retentive power in regard to water; for, though not wet or moist, in the common acceptation of the term, they sometimes contain four-fifths their weight of water, part of which may be squeezed out or dried off, when they become hard, brittle, or translucent, but again swell up and regain their former appearance on being immersed in water: this desiccation, however, always kills the part, if we perhaps except some among the lower orders of the animal creation, which are said to admit of being dried, and again revive when moistened. Under this view of the subject, therefore, a living animal may be regarded as a mass of organized matter, softened by water, probably to the amount of about three-fourths of its total weight. It has been ascertained that nothing but pure water gives the peculiar flaccidity and softness to which I have alluded: salt water, spirits, oils, and all other liquids, producing very different effects. When microscopically examined, these soft solids generally appear to be made up of small globular particles, of the nature of which, as far as muscular fibre is concerned, we shall have to speak afterwards.

When animal matter is subjected to *destructive distillation*, *ammonia* is a leading product; it is generally more or less saturated by carbonic, and occasionally by other acids, and often in the state of solid carbonate, or dissolved in water and contaminated by empyreumatic oil; the *salt* and *spirit of hartshorn* of old pharmacy, are products of this description, and the same are afforded by common bone, provided the *fat* has been previously separated; for animal, like vegetable fat, yields distinct products, being destitute of nitrogen. The *empyreumatic oil* formed in these processes, and often termed *Dippel's oil*, first passes over of a pale-yellow colour; it gradually becomes darker and thicker; but when redistilled with water, it is nearly colourless, of a penetrating odour, and gradually acquires a brown colour by exposure to air; it is alkaline, soluble in alcohol, inflamed by nitric acid, and by somewhat diluted nitric acid it

becomes resinous: it is soluble in hydrochloric acid, and precipitated by sulphuric and nitric acids; and by alkalis in an altered and apparently resinous state. The *tar* associated with this oil, has been before noticed as a source of eupion. This, and the oil, have been examined by Unverdorben, who has found in them no less than four distinct substances, which he considers as salifiable bases; namely, 1. *Odorin* (from *odor*), obtained by saturating the ammonia in the rectified oil, by nitric acid, then pouring off the oil, and distilling it in a water bath; the first portion which passes over is *odorin*; it has the concentrated odour of *Dippel's oil*, and combines with the acids, forming peculiar oily salts; it also forms double salts, in conjunction with several other salifiable bases. 2. *Animin* (from *animal*), is contained in the oil which succeeds the *odorin*; this, washed with water, saturated with sulphuric acid, and distilled, leaves *animin*; it is an oily fluid, having the odour of purified salt of harts-horn. 3. *Olanin* (from the first syllables of *oleum animale*), remains in the retort after the *odorin* and *animin* have distilled over; when washed with water, it resembles a fat oil; and when exposed to air it becomes brown, and is converted into *fuscin*. 4. *Ammolin* (from the first syllables of *ammonia* and *oleum*), is obtained from the crude or unrectified animal oil. Unverdorben has also described another salifiable base, which he obtains from animal empyreumatic oil, and which, as it forms crystallizable compounds with the acids, he has termed *krystallin*. The details of these researches, which are complicated, are contained in *Poggendorff's Journal* (viii. and xi.), and abstracts of them are given by Berzelius and Gmelin: it appears probable, that some of the supposed *educts* are produced by the various processes to which the oil is submitted for their separation; those who are engaged in researches connected with this subject, must consult the original papers.

The *gaseous products* of the destructive distillation of animal matter are extremely various, and easily modified in quality as well as quantity, by the manner in which the process has been conducted; the *charcoal* which remains after the separation of the volatile principles has been already repeatedly noticed as peculiarly adapted to the removal of colour, odour, and taste, from various solutions; and in consequence of the salts which it contains, and especially the phosphates, it resists incineration, and requires particular management when its incombustible contents are to be separated.

PUTREFACTION AND PRESERVATION OF ANIMAL MATTER.—The phenomena of animal putrefaction are extremely varied and complicated, and are easily affected by extraneous causes, such as temperature, air, moisture, and other agents. The changes which are thus produced in individual parts of animals, will be noticed in the sequel, but a few general observations may be made here, in reference chiefly to circumstances which influence or modify the process.

The influence of *temperature* is commonly known; every one is acquainted with the preservative powers of *cold*; and when animal matters are subjected to higher temperatures than those of warm climates, they undergo changes which do not come within the meaning of the term putrefaction. The greater number of animal substances are

indefinitely preserved at or below the freezing-temperature, and when slowly thawed, they generally regain their original characters; it is in this way that supplies of animal food are kept in a fresh state in many parts of the north of Europe, and that fish is preserved for the London market. A remarkable instance of the preservative power of cold was exhibited in the ancient elephant, found incased in a mass of ice, at the mouth of the river Lena, in Siberia.

Moisture is another essential to putrefaction; when flesh is carefully and thoroughly dried, either by a current of warm and dry air, or by other methods which do not alter its composition, it resists decay; it has thus occasionally happened that corpses have been preserved by accidental desiccation; and animal substances which are either naturally dry, or rendered so by art, retain their nutritive powers, and resume their former appearance when cautiously moistened. The various forms of gelatine, whilst kept dry, are imperishable; whilst in aqueous solution, or in their original humid state, they are the most perishable of the animal proximate principles, as skin and the varieties of tremulous jelly show.

Air, or at least *oxygen*, if not absolutely essential to, is a powerful promoter of putrefactive changes, and under certain circumstances, its exclusion indefinitely retards them*; it is thus, that in Appert's method of preserving animal and vegetable food, the substances are hermetically sealed in tin canisters, and then par-boiled; the included oxygen becomes converted into carbonic acid, or enters into other combinations. Oil, butter, suet, and such substances, are sometimes similarly effectual; and potted and preserved meats, when covered with a film of fatty matter, itself not prone to change, are in that way preserved from the contact of air. The manner in which various saline substances, and especially common salt, act, is not very clearly understood; it is partly by desiccation, or abstraction of moisture, and by a corrugating power over the animal fibre; and partly by the production of new compounds arising out of the neutral action of the salt employed, or its elements, upon the organic matter: the preservative powers of corrosive sublimate, sulphate of copper, acetate of copper, the corresponding salts of iron, and very many other similar compounds, are of the same description. These anti-putrefactives are generally coagulators of albumen; and alcohol, kreosote, and some of the dilute acids, have the same power, and are effective preservatives. Among vegetable products, the various forms of tannin act apparently by direct union with the animal fibre, producing combinations which are insoluble in water, which resist the joint agency of air, heat, and moisture, and which admit of desiccation. Sugar, which is sometimes employed as a substitute for salt, acts apparently by its affinity for water; and meat, which has been deprived by these or other means of only a part of its water, becomes infinitely less susceptible of putrefactive changes. The ancient Egyptians seem to have availed them-

* Hence, the rapidity of putrefactive changes in pure oxygen, and their retardation in gases which either do not contain it, or in which it is held by superior attractive power. Even under water, when oxygen is strictly excluded, putrefaction is greatly retarded and modified in its results. Meat immersed in water previously boiled to expel air, and then covered by a layer of oil, to prevent its subsequent absorption, may long be kept fresh: the presence of iron-filings and of sulphur in the water, assist in this species of preservation.

selves of almost all these methods of preservation in embalming their mummies, as appears from the researches of Dr. Granville and of Mr. Pettigrew, in reference to this curious subject.

When the flesh of animals is subjected to the action of running water, it is occasionally converted into a peculiar fatty matter, which has been termed *adipocere* (from *adepts* and *cera*); it somewhat resembles spermaceti in appearance, and was supposed to partake of the properties of *fat* and *wax*. In the year 1789, Fourcroy communicated to the Royal Academy of Sciences at Paris, a curious account of the changes sustained by the human bodies interred in the cemetery of the Innocents in that city; some of these had been piled, for a succession of years, closely upon each other, in large cavities containing from one thousand to fifteen hundred individuals. One of these graves, opened in Fourcroy's presence, had been full, and closed for fifteen years. When the coffins were opened, the bodies appeared shrunk and flattened, and the soft solids were converted into a brittle cheesy matter, which softened and felt greasy when rubbed between the fingers. The bones were brittle; and the texture of the abdominal and thoracic viscera no longer discernible, but lumps of fatty matter occupied their places.

It is not uncommon to find masses of this *adipocere* in the refuse of dissecting-rooms, especially when heaps of such offal are thrown into pits and wells, and suffered gradually to decay. The carcasses of cats and dogs, and other drowned animals, also often exhibit more or less of a similar change; and Dr. Gibbes (*Phil. Trans.*, 1794,) found that lean beef, secured in a running stream, underwent a change into fat in the course of three weeks. Fat, and the adipose parts of animals, also undergo a change in appearance and composition under similar circumstances: tallow becomes brittle and pulverulent, and may be rubbed between the fingers into a white soapy powder.

Gay Lussac, Chevreul, and some others, conceive that muscular fibre, skin, &c., is not convertible into *adipocere*, but that this compound results entirely from the fat originally present in the substance, and that the fibrin is completely destroyed by putrefaction. There are cases, however, in which the conversion of muscle and of fibrin into fat can scarcely be doubted (*Ann. of Phil.*, xii. 41), though the propriety of applying the term *adipocere* to such fatty matter may be questionable. The action of very dilute nitric acid upon some of the modifications of albumen is also attended by their conversion into an adipose substance.

The chemical properties usually ascribed to *adipocere* are the following: it fuses at a temperature below 100°; it dissolves in boiling alcohol, and the greater portion is deposited as the solution cools; the action of ether resembles that of alcohol; it is saponified by the fixed alkalis, but not by ammonia. It would appear, however, from Chevreul's experiments, that *adipocere* is not a mere modification of fat, or a simple product, but that it is a *soap* composed of margoric acid and ammonia.

Connected with the putrefactive changes of organic matter are those extraordinary products of death and of disease known under the name of *infectious* and *contagious matters*; their chemical nature is quite unknown, except in so far that they appear to possess the general characters of organic compounds, and are decomposed and resolved into harmless products by

certain chemical agents; amongst which heat, chlorine, and a few of the gaseous acids, are commonly resorted to for the purpose*. When articles of clothing or of merchandise which are infected with contagious matter are exposed for some time to a temperature of about 220° , they become disinfected, especially if at the same time subjected to a current of air. Washing in soap and water, boiling or steaming, are equally effective. In regard to *fumigation*, chlorine is the most effective agent; the mode of applying it, and some of its compounds, in these cases, has already been mentioned. In dissecting-rooms, and in the examination of dead bodies, too much care and attention cannot be paid to the prevention of the evil consequences to which various forms and applications of infectious and contagious products give rise. Their extraordinary power of exciting various and dangerous diseases, either by pulmonary or cuticular absorption, or other introduction into the living system, are too well known, but of their *modus operandi* we are utterly ignorant: sometimes they produce anomalous and uncertain effects; at others they have a tendency to create poisons in the living system, resembling themselves; the *inoculation* of diseases, as of the small-pox, &c., is a similar case, in which the introduction of the smallest fraction of a grain of poisonous matter excites new and morbid actions, and terminates in the throwing off from the system of a poison corresponding in its properties with that from which it was derived†. The theory of infection and contagion is mysterious and curious in the extreme, but its further consideration would be foreign to this work. Of another matter also connected with this subject, namely, the influence and production of *malaria*, of *marsh-miasma*, and other poisonous exhalations of organic, but principally of *vegetable* origin, we are equally ignorant; they chiefly produce that extraordinary disease, the *ague*, or *intermittent fever*; and their nature is obscure and unintelligible.

* In times of plague and other pestilence, the vicinity of smelting-furnaces was formerly resorted to as being least liable to the infectious visitation; the sulphurous and other acid fumes were doubtless the disinfectants. In such and similar situations, in chloride of lime manufactories, and in other chemical works, an immunity from certain diseases is consequently enjoyed, though others are sometimes engendered. It seems not impossible that the freedom which London enjoys from the spread of malignant diseases may, in part, be ascribed to the products of the combustion of coal, which always taint its atmosphere; the drainage, and the copious supply of water, contribute, however, essentially to the health of its inhabitants, for [the effluvia from the offal of large cities, if not speedily and effectively cleared off, is, of course, productive of infinite mischief; even in London, the construction and management of the *sewers* requires much reform, and

were it not for the *water-companies*, their evils would be more evident.

† Perhaps one of the most remarkable properties of some forms of infectious matter, is its permanency; retaining, as is frequently the case, its peculiar powers for an indefinite period. Of this, the preservation and transmission of *dried* variolous and vaccine matter is a familiar instance. The infection of *scarlet fever* is sometimes retained for weeks and months by articles of wearing-apparel; in one instance, after a malignant form of that disease had prevailed in a house, it was fumigated with chlorine and white-washed, and every article of furniture and clothing cleansed and fumigated, with the exception of a handkerchief which had been accidentally overlooked, and to which the appearance of the disease, after a period of two months, was probably attributable. Blankets and woollen goods seem especially retentive of such poisons, and in all doubtful cases should be burned.

§ I. OF THE BLOOD.

IN the higher orders of animals, the blood is of a red colour; florid and approaching to scarlet in the arteries, and deep purple in the veins. The specific gravity of the blood varies between 1·050 and 1·070, and its temperature in the healthy human body is about 98° or 100°. It has an unctuous or somewhat soapy feel, a slightly nauseous odour, and saline taste. It appears homogeneous, or uniform, whilst circulating in its vessels, or immediately upon its removal from them; but when examined by a microscope, it is seen to consist of numerous red spherical particles floating about in a colourless transparent fluid; the former having been termed the *red globules**, the latter the *serous portion*, or *liquor sanguinis*. The accounts given by microscopical observers of the appearance and characters of the red globules vary; they seem to consist of a central or colourless nucleus, enveloped in a film of colouring matter, the former insoluble, the latter soluble in water; they are said to be spherical in mammiferous animals, and elliptical in birds and reptiles; but upon this subject I must refer to physiological authorities, and especially to the observations of Mr. Bauer detailed and illustrated in Sir E. Home's *Lectures on Comparative Anatomy*.

Under ordinary circumstances, the blood, soon after it has been drawn from its vessels, gelatinizes or *coagulates*, and the jelly, or coagulum, gradually separates into two parts; a liquid *serum*, and a soft clot or *crassamentum*. In the act of coagulation, the globules apparently coalesce and throw off the colouring matter, which is generally diffused equably through the crassamentum so as to give it an uniform red colour; sometimes, however, it subsides, leaving a stratum of colourless coagulum, which, in inflammatory disorders, is called the *buffy coat* of the blood.

It is stated that blood, if rapidly frozen before it has time to coagulate, may be retained for an indefinite time in the frozen state, but that when thawed, it first liquifies, and then coagulates as usual; the coagulation is, at all events, much interfered with by temperature. Blood drawn from a vein in the arm at the temperature of 53°, coagulates in 4·5 minutes; at 98°, in 2·5 minutes; at 120° in 1 minute. Blood which coagulates in 5 minutes at 60°, remains fluid for 20 minutes at 40°, and requires 60 minutes for complete coagulation at that temperature. (SCUDAMORE *on the Blood*.) When blood is received into a close vessel, its coagulation is somewhat retarded; it is accelerated in the exhausted receiver of the air-pump. When drawn in a full stream, it coagulates more perfectly and more rapidly than when in a very small stream. It appears probable that, in the act of coagulation, the temperature of the blood is very slightly increased, consistently with the laws of latent heat. These are, I believe, the principal facts which have been ascertained upon this subject; they throw no light upon the *cause* of the coagula-

* It was supposed that the colouring globules were inherently red and soluble in water, but it has been shown by Dr. Young, that the effect of water is to dissolve the colouring matter only, leaving the globule colourless; in this state the

globular particles appear to have the properties of albumen. The diameter of the globules in human blood varies from $\frac{1}{100000}$ to $\frac{1}{10000}$ of an inch. (*Remarks on Blood and Pus*, in Dr. YOUNG'S *Medical Literature*.)

tion*. The ratio which the clot bears to the serum is variable, and partly dependent upon the shape of the vessel in which the blood is contained: "Two portions of blood were drawn from the same person, one being received and allowed to coagulate in a pear-shaped bottle, and the other in a pint basin; and the ratio of serum to clot was as 1000 to 1292 in the former, and as 1000 to 1717 in the latter. In fact, when a mass of coagulating blood is contained in a spherical vessel, the particles of fibrin, being little removed from a common centre, are more powerfully attracted towards each other, yield a denser clot, and squeeze out more serum than when the coagulation takes place in a shallow wide basin, where the particles are spread over a large surface; the clot of the former is compact and small; while that of the latter, being spongy, and hence retaining much serum within it, is large and abundant, though the actual quantity of solid matter is the same in both." (Dr. B. BABINGTON, quoted by Dr. Turner.)

The spontaneous coagulation of the blood, and its resolution into serum and coagulum, forms, as it were, a step towards its analysis, and naturally leads to the separate examination of these, its apparent proximate components.

SERUM OF THE BLOOD.—This is the pale, straw-coloured, or greenish-yellow liquid, which gradually oozes out of the crur or crassamentum; it feels soapy, and has a saline taste, and a specific gravity = 1·027 to 1·030 at 50°. It usually constitutes about three-fourths of the blood, the pressed coagulum forming about one-fourth; it is *alkaline* to tests, slowly reddening turmeric, and rendering the blue of violets green; the readiest test of its alkalinity is litmus paper reddened by acetic acid; to this it immediately restores the blue colour. When the serum is heated to about 150°, it becomes a soft solid, coagulating into a translucent mass, which, upon the continuance of heat, becomes more opaque, and gives out a small quantity of a yellowish alkaline liquid, which has been termed *serosity*; this characteristic property is due to the presence of *albumen*, a most important proximate animal principle; the serum also contains a small but variable portion of *fat*, and of saline substances.

Marcet and Berzelius have each given an analysis of the serum of human blood; the following are their results. (*Medico-Chirurgical Transactions*, vol. ii.; *Annals of Philosophy*, vol. ii.)

	Marcet.		Berzelius.
Water	900·0	Water	905·0
Albumen	86·8	Albumen	80·0
Hydrochlorates of potassa and soda	6·6	Hydrochlorates of potassa and soda	6·0
Muco-extractive matter	4·0	Lactate of soda, with animal	} 4·0
Carbonate of soda	1·65	matter	
Sulphate of potassa	0·35	Soda and phosphate of soda, } 4·1	}
Earthy phosphates	0·60	with ditto	
	1000·00	Loss	0·9
			1000·0

* The cause of the coagulation of the blood is unexplained; it is true that it apparently consists in the aggregation of its globules, but we are ignorant of what it is which prevents this effect in one case and promotes it in another; why the blood remains fluid whilst cir-

culating, and under other circumstances; and why it occasionally coagulates, *when required so to do*, as in hæmorrhage, to plug up the bleeding vessel, &c. We have no proof that the blood either receives or emits anything essential to its coagulation.

ALBUMEN.—This substance, which is the leading ingredient of the blood, occurs in two states, liquid and solid; in the former state it is contained in the serum, and in many of the secretions; in the latter it constitutes a part of the crassamentum, and of almost all the solids of the animal fabric, such as muscle, bone, cartilage, tendon, ligament, and membrane; it is presented to us, in considerable purity, in the *white of egg*, whence the generic term, *albumen*, and it is from this source, and from the serum of the blood, that we chiefly obtain it for the purposes of experiment. I shall here describe the leading properties of albumen, and afterwards refer to its principal modifications.

The white of egg may be regarded as a combination of albumen with water; it contains small quantities of saline substances, which are inseparable in its liquid state. When it is evaporated at a temperature below 120° , it dries into a brittle, shining, transparent substance, of a pale yellow colour, inodorous and tasteless. Its ultimate constituents, exclusive of saline matters and a trace of sulphur, are carbon, hydrogen, nitrogen, and oxygen; of these the relative proportions have been determined by Gay Lussac and Thenard, who analyzed the white of egg dried at 212° ; and by Dr. Prout, who employed the dried serum of slightly-inflammatory blood; the following table shows its theoretical composition as contrasted with the experimental results:—

	Gay Lussac.				Prout.
Carbon	8	48	51.61	52.883	50.00
Hydrogen	7	7	7.53	7.540	7.78
Nitrogen	1	14	15.05	15.705	15.55
Oxygen	3	24	25.81	23.872	26.67
Albumen	1	93	100.00	100.000	100.00

White of egg, when heated to about 150° , *coagulates*, that is, becomes a white, translucent, and somewhat elastic substance, which, when cautiously dried, shrinks up and assumes the appearance of horn, becoming tough, yellowish, and insoluble in water. 2 parts of white of egg and 1 of water entirely coagulate when duly heated; equal parts remain, under the same circumstances, semi-fluid; a mixture of 1 part of white of egg and 10 of water becomes opaque, but is not coagulated; and a milkiness is perceptible when the albumen only forms a thousandth part of the solution. (Bostock, *Nicholson's Journal*, xiv., and *Med. Chir. Trans.*, i. and ii.) Fresh-laid eggs, and those which have been oiled upon the surface, do not perfectly coagulate when put into boiling water, in consequence, probably, of the dilute state of the albumen. 100 parts of the fresh albumen of the egg, when carefully evaporated in vacuo, leave a residue = 15 parts. 100 parts of the coagulated white of a duck's egg (dried in vacuo with sulphuric acid) leave 13.65 parts, which, steeped in water, acquires its original appearance, but in four days only took up 68 of water, though it had lost 86.35. (CHEVREUL, *Mém. du Muséum*, vii. 180; *Ann. de Ch. et Ph.*, xix. 46.)

When liquid albumen is made part of the voltaic circuit, it presents appearances dependent upon the power used, which, when considerable, excites so much heat as to coagulate it; but with a feeble power, and the poles sufficiently distant, coagulation ensues most plentifully at the negative platinum-wire; a coagulum also forms at the positive wire,

where acid is sparingly evolved. These phenomena are much interfered with by the evolution of gases at the respective poles, which occasion a froth, and the appearance of more extensive coagulation than actually occurs. (BRANDE, *Phil. Trans.*)

When coagulated white of egg is boiled for several hours, it shrinks up and becomes hardened, communicating traces of animal matter to the water. Heated by high-pressure steam in a copper digester to 400° , it blackens the interior of the vessel, and dissolves, leaving a small residue of unaltered albumen. The solution is brown, and has the odour of boiled meat (from osmazome?). This action deserves further investigation. (GMELIN, *Handbuch der Theoretischen Chemie*, ii. 1053. 3rd ed., Frankfort, 1827.)

White of egg soon runs into putrefaction, and evolves sulphuretted hydrogen. The serum of blood kept for two years in a well-stopped phial, blackened its interior, and became a stinking, pale, yellow liquid, still coagulable by heat, and containing hydrosulphate, carbonate, and acetate of ammonia, and a fetid volatile matter; a portion of yellowish-white purulent-looking matter, containing undecomposed albumen, remained at the bottom of the phial. Coagulated white of egg, even under water, long resists putrefaction.

One hundred parts of dried white of egg, subjected to destructive distillation, yielded carbonic acid, carburetted and sulphuretted hydrogen, hydrocyanic acid, carbonate of ammonia, partly in solution and partly sublimed, stinking volatile oil, and 14.9 of spongy difficultly-combustible charcoal, which, by incineration, left 2.21 of ash, composed of carbonate of soda, phosphate of soda, and phosphate of lime. (HATCHETT.)

Nitric acid, dropped into a solution of albumen, forms a white, flaky precipitate, which is more or less abundant according to the state of dilution of the solution, and which is soluble in ammonia and potassa. When coagulated white of egg is kept for some weeks in very dilute nitric acid, it acquires a yellow colour, and if digested in boiling water it dissolves, and has acquired the properties of gelatine, and is precipitated by tan and hydrochlorate of tin. (HATCHETT, *Phil. Trans.*, 1799.) Cold nitric acid, specific gravity 1.25, gradually tinges coagulated white of egg of a yellow colour, dissolving a little of it, and forming malic acid, with the evolution of nitrogen; its surface becomes tallowy, and, in twenty-four hours, it falls into a pale yellow powder, which is acid, and composed of nitric, nitrous, and malic acids, with albumen; when thoroughly washed with water, it becomes more neutral, and of an orange colour, still reddening litmus, and remaining insoluble in water, but soluble in caustic potash. (BERZELIUS, *Lehrbuch*, p. 38; Wöhler's Translation, Dresden, 1831.) When coagulated white of egg is digested in hot nitric acid, nitrogen, nitrous gas, carbonic acid, and hydrocyanic acid are formed, and a dark yellow solution obtained, which is precipitated by the addition of water and ammonia, and which contains malic and oxalic acids, bitter matter, and fat. (HATCHETT, *Phil. Trans.*, 1799.)

Sulphuric acid is a less powerful precipitant of albumen than nitric acid. Dilute sulphuric acid, dropped into an aqueous solution of albumen, occasions a precipitate which is soluble in excess of acid; ferrocyanuret of potassium throws it down. When coagulated albumen is

digested in sulphuric acid, very slightly diluted, it yields a deep crimson solution*. Coagulated serum, digested in sulphuric acid diluted with 6 parts of water, converts it into acid *sulphate of albumen*, which, whenedulcorated with cold water, becomes more neutral, and is soluble in warm water, forming a gelatinous solution, which is precipitated by sulphuric, hydrochloric, and nitric acids, and by the alkalis. (BERZELIUS, *Lehrbuch*.) Coagulated white of egg, digested in hot sulphuric acid, becomes carbonized without forming artificial tan. (HATCHETT.)

When a solution of recently-fused phosphoric acid (pyrophosphoric acid) is added to a solution of albumen, it occasions an abundant precipitate: the acid gradually loses this property, but again acquires it by fusion and ignition. (BERZELIUS.)

Hydrochloric acid occasions a precipitate in albuminous solutions, and entirely throws down the albumen when aided by heat; but the precipitate is soluble in excess of acid, and in ammonia and potassa. A hydrochlorated albumen may be formed in the same way as the sulphate. (BERZELIUS.) Coagulated egg-albumen, digested in hydrochloric acid, gradually acquires a purple colour. (HATCHETT.) Albumen, which has been precipitated by hydrochloric acid, often becomes reddish when collected and exposed upon a filter.

When coagulated seralbumen is digested in acetic acid, it becomes soft and transparent, and, aided by a gentle heat, dissolves with the evolution of a little nitrogen. This solution is precipitated by the alkalis, but a slight excess again renders it clear: it is also precipitated by sulphuric, nitric, and hydrochloric acids, and by ferrocyanuret of potassium. When this acetic solution of albumen is evaporated, it leaves a transparent sour residue, soluble in warm water acidulated by acetic acid. (BERZELIUS.)

Albumen is slowly soluble in liquid ammonia. In solution of potassa it becomes gelatinous, and yields a pale yellow-green solution, precipitable by acids and alcohol, and by acetic acid. Heated in liquid potassa, albumen evolves ammonia.

Alcohol and ether coagulate ovalbumen, but pure ether (free from alcohol) does not coagulate seralbumen. When serum is shaken with ether, it soon separates upon the surface, holding fatty matter in solution. (GMELIN.) Coagulated serum, digested in alcohol or ether, yields a solution of fatty matter.

Coagulated ovalbumen, when long boiled in water, becomes bulky and falls into pieces, and a small portion is dissolved: the filtered solution, evaporated at 212° , leaves a pale brown film, and is alkaline; it is rendered turbid by mineral acids, acetic acid, and tincture of galls, and by many metallic salts.

When albumen, which has been cautiously dried at a low temperature (without coagulation), is triturated with 4 parts of water, it yields a solution resembling fresh albumen.

A solution of the white of an egg in a pint of water occasions no precipitate in lime, baryta, or strontia water, nor in solution of sulphate

* According to Raspail, when sugar is previously dissolved in the sulphuric acid, the albumen is coloured purple, | which is deeper in proportion as the acid and sugar are in greater quantity.

of lime. Some of the neutral salts render it more or less turbid, and it is copiously precipitated by solution of alum. Nitrate, acetate, and subacetate of lead are precipitated by albuminous solutions. One part of fresh ovalbumen in 2000 of water, or one of dried albumen in 10,000 of water, is rendered turbid by subacetate of lead. A four-hundredth part of liquid, or a two-thousandth of solid albumen, is precipitable by corrosive sublimate. (BOSTOCK.) The precipitate is blackened by potassa, and consequently supposed to be a compound of hydrochlorate of albumen and calomel. But Lassaigne has shown (*Ann. de Ch. et Ph.*, LXIV. 90), that it is soluble in alkalis and acids, and in solutions of alkaline chlorides, iodides, and bromides, and that it is a compound, apparently definite, of bichloride of mercury and albumen, in the proportion 6.5 of the former to 93.5 of the latter, or, according to his equivalents, of 1 atom of bichloride and 10 atoms of albumen. The ready solubility of this hydrargyro-chloride of albumen, in several saline and other liquids, may in many cases prevent the efficacy of the test; and should white of egg be at any time used as an antidote to the poisonous effects of corrosive sublimate, chloride of sodium should be avoided, and vomiting excited as speedily as possible, in order to prevent the redissolution of the compound in the secretions of the stomach. Nitrate of silver, chloride of gold, and of platinum, also precipitate albuminous solutions. These precipitates are mostly triple compounds of acid, albumen, and oxide, and several of them are redissoluble in excess of liquid albumen.

Albumen is precipitated by tannin in the form of a yellow viscid combination. Water, holding a thousandth part of solid, or a two-hundredth of liquid, ovalbumen, becomes turbid after some hours by the addition of a solution of galls containing 2.5 per cent. of solid matter. (BOSTOCK.)

The above are the principal chemical properties of liquid and solid albumen, as obtained from the egg and from serum of blood; several of their modifications will be noticed under other heads, such as *Fibrine*, *Milk*, *Bile*, &c.

The cause of the coagulation of albumen is, in many cases, obscure and even inexplicable. It appears that in some cases the acids by which it is coagulated enter into combination with it, so as to form insoluble compounds; the same change probably happens with certain metallic salts, and with tan; its coagulation by alcohol has been ascribed to the abstraction of water. Having remarked the copious coagulation of [albumen at the electro-negative pole in the voltaic circuit, I was induced to ascribe the fluidity of albumen to combined soda, the evolution of which seemed to cause its solidification; and it appeared possible that the acids, and even alcohol, might also occasion coagulation by the abstraction of soda; and that its more enigmatical coagulation by heat only, might be ascribed to the transfer of soda from the albumen to the water. It has been objected to this statement that the addition of alkali to coagulated albumen does not reproduce liquid albumen, and that acetic acid causes no coagulation; but when albumen is once coagulated, its properties are essentially modified, and acetic acid, or even acetate of soda, appear to form soluble compounds with it. (GMELIN.) Dr. Turner (*Elements of Chemistry*) supposes that albumen combines directly with water at the moment of

being secreted, at a time when its particles are in a state of minute division; but as its affinity for that liquid is very feeble, the compound is decomposed by slight causes, and the albumen thereby rendered quite insoluble. The organization of albumen may certainly be concerned in its singular properties with respect to many coagulants: there are several albuminous fluids, which we shall hereafter refer to, which contain globules resembling those of the blood. In the voltaic coagulation of albumen, that which separates at the positive pole contains globules, which, under the microscope, resemble the blood globules deprived of their colouring matter. (PREVOST and DUMAS, *Ann. de Ch. et Ph.*, xxiii. 52.)

The readiest tests of the presence of albumen in fluids are its coagulation by heat, alcohol, and acids; when it is too dilute for such detection, it may be subjected to voltaic electricity, or tested by corrosive sublimate, or by ferrocyanuret of potassium; the alkali should, in the latter case, be previously neutralized by acetic acid. It would appear, from Orfila's experiments, that white of egg is an antidote to the effects of corrosive sublimate when taken into the stomach, and that, if administered in sufficient quantity immediately after the reception of the poison, it prevents the progress of the symptoms. The white of one egg appeared sufficient to render four grains of the poison ineffective.

The readiness with which some metallic oxides are received into the system may perhaps be ascribed to their affinity for albumen, with which some of them form compounds not easily decomposable, and in which the metallic oxide cannot be detected by the usual tests, till they have been subjected to heat sufficient to decompose the organic matter. Mercury and silver are thus, in certain cases, detected in the secretions and excretions.

CRASSAMENTUM. COAGULUM.—These terms are applied to that part of the blood which spontaneously coagulates, and gradually contracts into a more or less dense mass. When cautiously removed from the serum in which it is immersed, and of which it always retains a considerable proportion, it may be regarded as principally consisting of *fibrin* and *colouring matter*.

FIBRIN.—This substance may be separated from the serum and colouring matter, by washing it in repeated portions of cold water; or by stirring recently-drawn blood with a stick, to which the coagulum will adhere, and it may then be conveniently washed in running water, till the serum and colour are extracted, and the fibrin remains in the form of a nearly colourless and fibrous substance, insoluble in cold water. Berzelius obtains fibrin by cutting the clot of blood into thin slices, drying them upon folds of blotting paper to absorb the serum, and then washing with water till all soluble matters are extracted. The fibrin, however, still retains a little fat, for the removal of which it must be digested in ether, or in warm anhydrous alcohol.

Another mode of obtaining pure fibrin sometimes presents itself, which consists in removing the colourless layer which is occasionally observed upon blood drawn in inflammatory diseases, and termed the *buffy coat*; when this is washed, digested in alcohol or ether, and dried,

it may be considered as nearly pure fibrin: this substance appears to be identical with the part of blood termed *coagulable lymph*.

When fibrin is obtained by any of these means, it retains about three-fourths of its weight of water, which it loses by careful drying, and shrinks up into a translucent tough substance, very like horn; if its fat has not been separated, it is nearly transparent. When immersed in water it regains its original weight and softness; it has no smell or taste; when highly heated, it fuses, puffs up, burns, and leaves a spongy, shining coal. By destructive distillation it yields the usual products of azotised substances: the residuary coal is of difficult incineration, and amounts to about two-thirds per cent. of the weight of the original fibrin: the ash consists of phosphate of lime, a little phosphate of magnesia, and traces of iron and silica. The coal of the blood of the ox is more difficultly incinerated than that of human blood, in consequence of its containing more phosphate of lime.

Dried fibrin is insoluble in cold and in hot water, but, if long boiled, it shrinks, hardens, and becomes pulverulent; when the decoction is evaporated, it leaves a brittle yellow substance, of an agreeable flavour, and soluble in water; its solution is precipitated by infusion of galls, but it has not the other characters of gelatine; it has been termed *animal extractive*, and seems closely to resemble the substance which has been designated *osmazome*.

When fibrin is acted on by acids and by alkalis, it sometimes appears to perform the part of a base, and sometimes that of an acid. In sulphuric acid it swells up to a yellow jelly, but does not dissolve; heat is given out, and if the temperature is not kept down, the mixture chars and evolves sulphurous acid, but if kept cold, no such decomposition ensues. In water the jelly shrinks up, and when washed, so as to get rid of excess of acid, it dissolves in water and forms a solution, from which sulphuric acid again throws it down in its gelatinous form; there appears therefore to be a neutral and soluble, and an acid and insoluble, *sulphate of fibrin*. If the colouring matter has not been entirely abstracted these solutions are red*.

Cold nitric acid forms, with fibrin, a gelatinous combination, resembling the sulphate; further digestion in the acid renders it yellow, and it then appears to be a compound of fibrin with nitric and malic acids.

Phosphoric acid, recently ignited and dissolved, acts upon fibrin like sulphuric acid, but if the acid has been kept in solution for eight or ten days the fibrin swells up in it into a soluble jelly, which is not thrown down by excess of the acid.

Acetic acid converts fibrin into a substance, soluble in warm water, and yielding a gelatinous mass on evaporation, differing from *gelatin*. Evaporated to dryness, the fibrin remains opaque and insoluble. The other acids added to this acetic solution, throw down precipitates which

* According to Braconnot, when water is added to the recent sulphuric solution of fibrin, and the mixture boiled for a few hours, and then saturated by chalk, the filtered solution contains a peculiar white matter, which he terms *Leucine*. (*Ann. de Ch. et Ph.*, xiii.) This is probably a compound of fibrin and sulphuric acid.

are compounds of fibrin and of the added acid. Caustic alkali precipitates the fibrin, and, if added in excess, redissolves the precipitate.

Hydrochloric acid gelatinizes dry fibrin, and then dissolves it into a blue liquid, or purple, if not previously freed from colouring matter. No gas is evolved, and the solution, when diluted with water, lets fall a white precipitate which is a neutral *hydrochlorate of fibrin*, and has the general properties of the neutral sulphate: the remaining liquid retains its blue colour; saturated with ammonia, the colour disappears, and excess of ammonia renders it yellow: the blue colour, therefore, probably depends upon a new product.

Digested upon moist fibrin hydrochloric acid does not dissolve, but combines with it into the neutral hydrochlorate. Boiled in the acid, it is decomposed, nitrogen is evolved, and on evaporation a dark brown ammoniacal compound remains.

The acid solutions of fibrin give a white precipitate with ferrocyanuret of potassium, which at first is soluble, but becomes permanent on adding excess of the precipitant. It is a compound of cyanuret of iron, fibrin, and hydrocyanic acid; it is insoluble in dilute acids, but soluble in caustic alkali. The red ferrocyanuret of potassium (ferrosesquicyanuret) throws down a more soluble precipitate than the above. These precipitates are very characteristic of fibrin, and of seralbumen, ovalbumen, and lactalbumen, and serve to establish the analogy, if not identity, of those modifications of this animal principle.

Fibrin is soluble in caustic potassa, even when the solution is very dilute; it gelatinizes and then dissolves, and is precipitated, if not too dilute, by acids; a little sulphuretted hydrogen is always then evolved, which seems to indicate some further change.

Digested in alcohol, or in ether, fibrin yields fatty matter, which, according to Chevreul, is merely abstracted, but Berzelius regards it as a new product: it is soluble in alcohol, crystallizable, and reddens litmus.

The above account of the fibrin of the blood is chiefly abstracted from the works of Berzelius (*Lehrbuch*, iv., and *Medico-Chirurgical Trans.*, iii. 201.) Some of its other characters will be mentioned when speaking of *muscular fibre*.

The ultimate analysis of fibrin agrees, as might be expected, in its outline, with that of albumen; there is, indeed, every reason for regarding them as different species of one organic principle. The atomic views which have been given of these animal principles, I do not quote, inasmuch as their combinations are not sufficiently definite to give their equivalents, and as we have no criterion by which to judge of their absolute purity, especially as concerns their variable proportion of water. The following are the results of the analyses:

	Gay Lussac and Thenard.		Michaëlis.	
			<i>Venous.</i>	<i>Arterial.</i>
Carbon	53.360	. . .	51.374	. . . 50.440
Hydrogen	7.021	. . .	7.254	. . . 8.228
Oxygen	19.685	. . .	23.785	. . . 24.065
Nitrogen	19.934	. . .	17.587	. . . 17.267
Fibrin	100.000		100.000	100.000

COLOURING MATTER OF THE BLOOD. HÆMATOSYN. HÆMACHROME.—

It is extremely doubtful whether the colouring matter of the blood can be effectually separated from other principles, and especially from albumen. By stirring blood during coagulation, a considerable portion is diffused through the serum, from which it afterwards subsides. Vauquelin advises the digestion of the coagulum, drained of serum, in dilute sulphuric acid at a temperature of 160° . The liquid, filtered while hot, is to be evaporated to half its bulk, and nearly saturated with ammonia; the colouring matter falls, and is to be washed and dried. (*Ann. de Ch. et Ph.*, i.) But in this process the hæmatosyn has probably undergone some change.

The chemical properties of the colouring matter of the blood seem to show that it is a peculiar animal principle. It is soluble in cold water, and the solution, when boiled, deposits a brown sediment of altered colouring matter. Hydrochloric, dilute sulphuric, and several of the vegetable acids, and the caustic and carbonated alkalis, readily dissolve it, and form solutions of different tints of red, and of a peculiar greenish hue when viewed by transmitted light. Nitric acid instantly renders these solutions brown, and decomposes the red principle. These and other properties (*Phil. Trans.*, 1812), led me to regard the colouring matter of the blood as a *distinct proximate principle* of animal matter, independent of the presence of iron, to which metal its peculiarities were at one time referred by Fourcroy and Vauquelin; and the latter verified my conclusions in the above-quoted memoir. Berzelius, whose labours in animal chemistry are at once refined and extended, has arrived at different conclusions; according to him the crassamentum of the blood consists of

Colouring matter	64
Fibrin and albumen	36
	<hr/>
	100

The colouring matter, when incinerated, affords a residue consisting of

Oxide of iron	50.0
Subphosphate of iron	7.5
Phosphate of lime with magnesia	6.0
Lime	20.0
Carbonic acid and loss	16.5
	<hr/>
	100.0

The iron he regards as contributing to the red colour of the blood, and a hint has been thrown out by Dr. Ure as to the possibility of its being derived from sulphocyanuret of iron.

Berzelius examined the solution of the colouring matter obtained by washing the coagulum, deprived of its serum, in water.

The strong filtered aqueous solution, thus obtained, is dark brownish-red, and becomes brighter by dilution: evaporated at 100° , it leaves a dark residue, soluble in water, but a boiling heat changes, and renders it insoluble. Chlorine darkens the concentrated solution, and then gradually destroys its colour: alcohol coagulates and renders it insoluble: the acids generally decompose it. Acetic acid heightens the colour of the

solution of hæmatosyn, but does not precipitate it: on neutralizing the acetic acid by potassa, the hæmatosyn is precipitated. Weak alkaline solutions act nearly similarly. Sulphuretted hydrogen renders the solution of hæmatosyn first violet, then green, and the red colour is not restored either by alkali or acid. Hæmatosyn is thrown down of a *red* colour by acetate of lead, sulphate of zinc, and corrosive sublimate; and *brown* by nitrate of lead, of silver, and of copper, and by chlorides of gold and of platinum.

The experiments of Dr. Stevens and of Mr. P. Squire, have further illustrated the peculiar nature of hæmatosyn. One of its most striking characters is the change of tint which it apparently suffers by the action of air, and which is well seen in the exposure of venous blood to the contact of air, or of oxygen. The colouring matter of the blood is also rendered florid and brilliant, even when in its blackest venous state, by almost all neutral salts; with sulphate of soda, for instance, or with nitrate of potassa, the effect is extremely striking. Acids and alkalis generally render the hæmatosyn black; tartaric, citric, and even carbonic acid produce this effect: they exert more or less solvent power over it, and their solutions are dingy, and often nearly black, by reflected light, but of a peculiar green tint by transmitted light, the intensities of these colours depending upon their states of dilution. Acid salts, and basic salts, act more or less as free acids or alkalis. In neutrosaline solutions, on the other hand, hæmatosyn is insoluble, and if its dark coloured acid, and alkaline solutions be so mixed as accurately to neutralize each other, the hæmatosyn falls, and acquires a florid tint. To observe the action of acids, alkalis, and salts, upon hæmatosyn, to the utmost advantage, the blood should not be suffered to coagulate, but received, whilst flowing, into the acid, alkaline, or saline solution. These facts have been applied by Dr. Stevens to explain the changes of colour which blood suffers in passing from the venous to the arterial state. (*London Medical Gazette*, April, 1834.) He shows, that venous blood contains carbonic acid, and that it gives it off when drawn from the arm into a vessel filled with hydrogen, all contact with air or oxygen being carefully avoided, so as to preclude the formation of carbonic acid by the union of carbon in the blood with the oxygen of the air: that this carbonic acid blackens the hæmatosyn, and that its red colour is restored by its removal, when the saline matters of the blood render it florid: that the change of arterial to venous, or of florid to black blood, occurs in the extreme ramifications of the vessels, or in their capillary anastomoses, for the blood is arterial in the extreme arteries, and venous in the extreme veins: Dr. Stevens also infers that arterial blood contains atmospheric air, or air more abundant in oxygen than that of the atmosphere; and that the removal of the carbonic acid in the lungs is effected by a peculiar attractive power of oxygen for carbonic acid, taking place through the membrane of the lungs; he concludes, and adduces satisfactory experiments in proof of the conclusion, that the change of venous into arterial blood, is not the result of the absorption or combination of oxygen, but of the loss or abstraction of carbonic acid by or from the black blood; the *blackening* cause being thus removed, the saline matter present becomes efficient as the *reddening* cause; for Dr. Stevens has proved that if the salts be abstracted from the

colouring matter, it retains its black colour, notwithstanding the loss of carbonic acid; and that a piece of highly-florid coagulum becomes black when its salts are washed out, and can only again be rendered florid by the addition of saline matter. All these facts have, of course, important bearings upon the theory of respiration*.

To the statement which I have now given of the nature and properties of the components of the blood, the following curious facts respecting the *odour* of different kinds of blood have been added by M. Baruel. Whilst preparing the colouring matter of blood according to M. Vauquelin's process, the clot of ox-blood was heated with a large excess of sulphuric acid of moderate strength, on which occasion a strong odour of beef was observed. Some time after, having occasion to operate upon the blood of a man who had taken opium, the fluid was first coagulated by heat, and divided, after which it was boiled with weak sulphuric acid: immediately so strong an odour of the sweat of man was evolved, as to infect the whole laboratory, and render it necessary for the persons to leave the place. This and the former fact combined, induced M. Baruel to extend his experiments on these subjects, and the following are the results he obtained.

i. The blood of each species of animal contains a principle peculiar to each. ii. This principle, which is very volatile, has an odour resembling that of the sweat, or the cutaneous or pulmonary exhalation of the animal from which the blood was taken. iii. In the blood, this volatile principle is in a state of combination, its odour being then insensible. iv. When the combination is broken, this principle is volatilized, when it is easy to recognise the animal to which it belongs. v. In each species of animal, this principle is more decided, or has more intensity of odour in the male than in the female; and in men, the colour of the hair accompanies certain variations in this principle. vi. This principle is in a soluble state in the blood, and may be found, therefore, either in the unaltered blood, or after the fibrin has been removed, or even in the serosity of blood. vii. Of all the means of separating this principle, concentrated sulphuric acid has succeeded best.

To obtain these results, it is only necessary to put a few drops of blood, or the serum of blood, into a glass, to add concentrated sulphuric acid to the amount of one-third or half as much as of blood, and to stir the whole together with a tube; the odoriferous principle is immediately

* Dr. Stevens observes that there is an apparent exception to the blackening effect of acids on the blood. "As the carbonates are weaker salts than those that are formed with fixed acids, and as the alkaline carbonates form a considerable portion of the natural saline matter of the blood, it follows that when we add an acid solution that is just strong enough to convert this weaker into a stronger salt, we then brighten the colour. It is for this reason that a salt with a slight excess of acid increases the arterial appearance. It is also for

the same reason that there is generally an increased glow of red when we first mix any of the acids with the warm blood; but if we add a very small proportion more of a fixed acid than is just sufficient to convert the alkaline carbonates into neutral salts, the red colour is so irretrievably destroyed by the excess of acid, that with the addition of a little water, the whole is converted into a fluid which exactly resembles the black vomit." (*Observations on the Blood*, by WILLIAM STEVENS, M.D.; London, 1832.)

rendered evident. By these means, M. Baruel can readily distinguish the blood from the following sources.

i. That of a man disengages a strong odour of the perspiration of man, which it is impossible to confound with any other. ii. That of a woman, a similar odour, much weaker, and resembling the perspiration of woman. iii. That of the ox, a strong odour of beef. iv. That of the horse, a strong odour of the perspiration of the horse. v. That of the sheep, a strong odour of wool impregnated with the perspiration of that animal. vi. That of the dog, the odour of the transpiration of a dog. vii. That of a pig, the disagreeable odour of a piggery. viii. That of a rat, the bad odour belonging to the rat.

The same result has been obtained with the blood of various kinds of birds, and even with the blood of a frog, which gave the strong odour of marshy reeds, &c., and with that of a carp, which gave a principle smelling like the mucus which covers the bodies of fresh-water fish.

Upon trials made to ascertain whether spots of blood could be distinguished, and referred to their source, M. Baruel found, that to a certain extent, a pretty sure judgment could be given, even after fifteen days or more. The spotted linen is to be cut out, put into a watch-glass, and being moistened with a little water, is to be left for a short time at rest. When well moistened, a little concentrated sulphuric acid is to be added, and stirred about with a tube; then, by respiring near it, the odour may be perceived. M. Baruel is not sure that the distinction could be ascertained after more than fifteen days, and therefore recommends legal officers to allow of no delay in any experiments, which bear upon cases of judicial investigation.

A question has sometimes arisen as to the possibility of preserving blood, with its principal characters either unimpaired or little altered; the following facts will, perhaps, illustrate this point. In the month of May 1818, blood was drawn from the arm into six phials, each holding about two ounces; these were secured by good corks, which were cemented over, and put away in a closet where they remained till May 1833, a period of 15 years. Two of the phials were then opened. The blood was perfectly liquid without any appearance of coagulum; there seemed to have been no extraordinary evolution of gaseous matter, but it exhaled a nauseous and slightly-putrid odour, with a trace of sulphuretted hydrogen. It was of a dark-purple colour, but became florid-red and was coagulated upon the addition of a few drops of solution of corrosive sublimate; it was blackened and coagulated by acids; alcohol also coagulated it; and the action of acetic acid and of ferrocyanuret of potassium, resembled that upon fresh serum. The chief apparent change, was loss of power of spontaneous coagulation. Heat and electricity coagulated it.

Having enumerated the principal facts which bear upon the chemistry of the blood, I shall now subjoin the results of its analysis by Lecanu (*Ann. de Ch. et Ph.*, LXVII. 54), to whom we are indebted for much curious information and laborious research in this difficult subject. He considers the venous blood of man, in its normal state, as composed of

Serum	869
Globules	131

or of

1000

Water	790·3707	
Oxygen	}	10·980
Nitrogen		
Carbonic acid		
Extractive matters		
Phosphorized fat		
Cholesterine		
Serotine		
Free oleic acid		
Free margaric acid		
Chloride of sodium		
Chloride of potassium		
Chloride of ammonium		
Carbonate of soda		
Carbonate of lime		
Carbonate of magnesia		
Phosphate of soda		
Phosphate of lime		
Phosphate of magnesia		
Sulphate of potassa		
Lactate of soda		
Salts of fixed fatty acids		
Salts of volatile fatty acids		
Yellow colouring matter		
Albumen of the serum	67·8040	
Globules	130·8453	
	1000·0000	

He considers the globules as constituted of

Fibrine	2·9480
Hæmotosine	2·2700
Albumen	125·6273

130·8453

The fluctuations in the composition of healthy blood he represents as follows:—

For the water.	For the saline extractive and fatty matters.	For the albumen of the serum.	For the globules.
from 805·263 to 778·625	from 14·000 to 8·870	from 78·120 to 57·890	from 148·450 to 115·850

Lecanu has also given the following statement of the comparative analysis of blood drawn from ten men and ten women.

	Males.	Females.
Water	789·32	804·37
Albumen	67·50	69·72
Saline and extractive matter	10·69	9·95
Red globules	132·49	115·96
	1000·00	1000·00

According to Lecanu the proportion of the red globules may be regarded as a measure of the vital energy, for the action of the serum and of the globules upon the nervous system is very different; the former scarcely excite it, while the latter do so powerfully: it would also appear that every cause which tends to diminish the mass of blood tends at the same time to a diminution of the relative proportion of the globules; hence the effect of bleeding, uterine evacuations, &c.

In reference to the difference between arterial and venous blood, Lecanu concludes that the colour and odour of the former are more intense, that it has more tendency to coagulate, and contains more globules, less water, and more free oxygen in proportion to its carbonic acid.

Comparative experiments have been made on the blood of different animals by Prevost and Dumas, by Tiedemann and Gmelin, and by other physiologists and chemists, for the details of which I must refer to their respective works: the general results are, that the globules vary in size and form, and that the components differ somewhat in their relative proportions, rather than in their essential qualities. In all animals the relative proportion of the aqueous to the solid part of the blood is liable to fluctuation, even in the healthy state, hence the discrepancies in its specific gravity; it is probable also that the quantitative if not the qualitative composition of the blood varies in different vessels and different parts of the body, hence, perhaps, the slight difference observed in blood abstracted by cupping, as compared with that drawn from the arm, and hence too, there is a difference in the blood drawn from a vein in the arm and that from a vein returning from some large gland, such as the kidney or liver.

BLOOD IN DISEASE.—We are but imperfectly acquainted with the changes in the composition of the blood which are the result of disease. The morbid changes of the blood resolve themselves into those dependent upon excess or deficiency of its usual components, and those in which foreign substances are detected in it; but the composition of the blood is such as to interfere in almost all cases with the nice indications of delicate tests, and the quantities of foreign matters which render the blood diseased in some cases are so small, as to elude very accurate observation. In cases in which the functions of the kidneys are much disturbed, urea is detected in the blood; and where the secretion of the urine is suspended, it is present in considerable quantity, and the source probably of the fatal consequences that ensue from that cause. Prevost and Dumas tied the renal vessels, and extracted the kidneys of a dog, and on the second day after the operation, they obtained no less than 20 grains of urea from 5 ounces of his blood. (*Ann. de Ch. et Ph.*, xxxiii. 90.) Urea has also been detected by Dr. O'Shaughnessy in the blood of patients suffering under Cholera, in which disease the renal functions are usually much disturbed. In jaundice, the colouring principles of the bile occasionally exist in the blood, and are discernible in the serum. It not unfrequently happens that the serum of the blood resembles whey, or milk and water; and sometimes it resembles cream; but such cases are very rare; these appearances depend upon the presence of fatty or oleaginous matter, which may be separated by agitation with ether. Drs. Traill and Christison procured 1 per cent. of fat from opalescent serum, and as much as 5 per cent. from serum which had the appearance of milk. (*Edinb. Med. and Surg. Jour.*, April, 1830.) In some nervous fevers of a typhoid character, the blood is said, during the increase of the disorder, to be more aqueous or thin than in health, and gradually to become more dense during its decrease. The state of the blood in Cholera has excited a good deal of attention. The peculiar whitish or whey-like discharge from the bowels, is said to contain albumen, and the salts of

the blood with particles of fibrin; the density of the blood itself is above the natural standard, it is of a remarkably dark colour throughout the system, and sometimes viscid, and incapable of coagulation, but at the same time deficient in saline matter. These appearances have been ascribed to various causes. According to Dr. Thomson, the blood in cholera is wholly unsusceptible of the usual influence of the air, and is consequently decidedly altered in its nature. Dr. O'Shaughnessy however found, that it did become florid when agitated with air, and that it emitted carbonic acid gas. Dr. Stevens ascribes the appearances to deficiency in saline matter, and successfully treated such cases, not only by the administration of solutions of common salt and of chlorate of potassa, but by the actual injection of solution of salt into the veins. Dr. Turner observes, that the most correct opinion perhaps is, that the blood of persons in cholera, in consequence of deranged arterial action, circulates sluggishly, and is therefore imperfectly arterialized, and that the dark colour may arise from that cause, independent of any diminution of saline matter, and may disappear, from an improved circulation, without the administration of salt; although there is no doubt that loss of saline matter increases the dark tint of the blood, and prevents it from acquiring the arterial colour. The secretion of a large quantity of saline fluid by the intestines in these cases, the decided deficiency of salts in the blood, and the relief afforded by restoring saline matter to the system, are, however, strong points in favour of Dr. Stevens's views. The substance ejected from the stomach in the last stage of yellow fever, and known under the name of *black vomit*, is blood blackened and coagulated by the free acid of the stomach.

Messrs. Andral and Gavarret in an elaborate paper on the influence of disease on the composition of the blood (*Ann. de Ch. et Ph.*, LXXV. 225), have arrived, among other interesting conclusions, at the following:—1. That in acute inflammations (phlegmatic) the fibrin of the blood is in excess, and that there is a disposition to its rapid formation. 2. That in febrile diseases (pyrexia), where any modification of the blood is perceptible, the relative proportion of the globules to the fibrin sustains an increase. 3. That in certain cachexia and diseases of debility there is a deficiency in the globules. 4. That in cases of albuminous urine the albumen of the blood sustains an equivalent diminution.

DETECTION OF BLOOD.—It is occasionally important in juridical inquiries, to distinguish between stains upon metal and linen arising from blood, and those from other sources. Orfila has given some useful information upon this subject.

Blood-stains on Steel. When the blade of a knife is stained by blood, it is *red* when the layer is very thin, but *brown* if thicker: heated to about 80°, the blood-spot peels off, leaving the steel tolerably clean; no such appearance arises from common rust, but something like it may be produced by the juice of fruits; in that case the blood-spot may be distinguished from that of vegetable juices, by collecting the portion which scales off, and heating it in a bit of glass tube closed at one end; it exhales the odour of animal matter and ammonia, and the latter may be recognised by its *alkaline* reaction on test-paper: any of the vegetable stains would, under such circumstances, exhale *acid* fumes; and mere

rust would either give out nothing, or at all events, the slightest possible trace of ammonia. Where it is practicable, the following process is more exact; the stained steel is immersed in water; the hæmatosyn and some albumen gradually dissolve, and leave the fibrin on the blade, from which it may be removed by the nail; red streaks form in the water, which becomes red at bottom: divide this red part into several portions; to 1 add chlorine; it becomes green, then colourless, and then deposits white flakes. To 2 add ammonia, which does not alter the colour, when from blood, but if from any ordinary dye-stuff, it becomes purple. Into 3 drop nitric acid; it becomes pale-gray. Into 4 a drop or two of infusion of galls; it does not alter the colour, but occasions a slight cloud. Heat 5 till it boils, when it either deposits flakes, or becomes opalescent. Of these tests, nitric acid and infusion of galls are the most delicate; should rust of iron have mingled itself with the liquid, it may be separated by filtration.

Blood-stains on Linen, &c. Suspend the piece of linen in a little water; the fibrin remains upon it, and may be detected by the evolution of ammonia, if linen or cotton, on the application of a sufficient degree of heat, in a small tube; but the hæmatosyn and some albumen are dissolved or extracted; test the coloured solution as above directed. Should the blood have coagulated upon one piece of linen, and then have gone through, so as to discolour another, no fibrin will be found on the latter. It is possible that a solution of madder, or some such colouring matter, in a serous or albuminous liquid, might lead to deception; but in this case the stain upon the linen would not be so easily removed by water, and the red solution would become yellow by acids, and violet by alkalis; a mixture of serum and the red of madder is rendered yellow, and does not remain red, on adding infusion of galls.

§ II. MILK.

THIS fluid, secreted by females of the class *mammalia* for the nourishment of their young, is a white, translucent, aqueous emulsion, containing oil, curd, a species of sugar, mucus, salts, and a free acid*, so that fresh milk slightly reddens litmus. Cows' milk has been principally examined. When carefully evaporated, it leaves from 10 to 12 per cent. of residue, but many circumstances interfere with this average. The specific gravity of skimmed milk is 1·033; that of cream 1·024: they consist, according to Berzelius, of

Skimmed Milk.		Cream.	
Water	928·75	Butter	4·5
Caseous matter or curd, with a trace of butter	28·00	Curd	3·5
Sugar of milk	35·00	Whey	92·0
Hydrochlorate and phosphate of potassa	1·95		100·0
Lactic acid, acetate of potassa, and a trace of } lactate of iron	6·00		
Earthy phosphates	0·30		
	100·00		

* This acid is the *lactic acid*. It is abundantly generated during the spontaneous changes which milk undergoes in becoming *sour*.

These can, of course, only be regarded as the average quantities, for, to say nothing of the different density of the milk of different breeds of cows, it varies in the relative proportion of its solid contents at different periods after the birth of the young*; and also with the food of the animal. Subtracting the curd from the contents of the milk, the residue constitutes *whey*.

CREAM arises from the gradual separation of the lighter suspended matters, and the shallower the vessel the sooner it separates. When milk is kept for 5 or 6 days at the temperature of about 33° , it evolves nearly the whole of its cream; the residue looks like milk and water. By *churning*, cream is separated into *butter* and *butter-milk*†; during this process, the temperature of the cream is slightly elevated, a little oxygen is absorbed, and acid produced; but this change is not essential to the separation of the butter, which takes place when air is excluded.

BUTTER is an oily matter, retaining, in its ordinary state, a little curd and whey; it liquifies at 98° ; if melted in hot water, washed, strained, and then allowed to concrete, its impurities are separated; it is less apt, in this state, to grow rancid. 100 parts of alcohol, of $\cdot 822$, dissolve $3\cdot 42$ of butter. Butter is easily saponified, requiring for the purpose not more than $0\cdot 4$ of hydrated potassa: it yields $88\cdot 5$ per cent. of concrete fixed acids, in which a little stearic acid, $11\cdot 85$ glycerine, and three distinct volatile acids, are included. Butter also includes three distinct species of fatty matter; namely, a stearin, an elain, and a third substance, *butyrin*, which produces the volatile acids of its soap. (CHEVREUL.) The relative proportions of these fats vary, whence the varying consistency of butter. The *stearin of butter* may be obtained by expression, or by deposition from its hot alcoholic solution; it is white, crystalline, and fusible at 112° . 100 parts of boiling alcohol, of $0\cdot 822$, dissolve only $1\cdot 43$ parts of it; when saponified, it yields $0\cdot 945$ of fat acid, fusible at 112° , $0\cdot 072$ glycerine, and traces of volatile acids. The *elain* of butter is very difficultly separable from butyrin: Chevreul endeavoured to obtain it by keeping purified butter for a long time at a temperature of about 70° ; the elain and butyrin gradually liquified, and were poured off from the stearin in the form of an oil, specific gravity $= 0\cdot 922$ at 66° . 100 parts of boiling alcohol, of $0\cdot 822$, dissolved 6 parts. Digested for twenty-four hours with anhydrous alcohol at 66° , it yielded a solution, which, when poured off from the residue, and distilled in a water-bath, left a sour oil, smelling of butter, and consisting of butyrin with a little elain; the acid was abstracted by washing with a little magnesia and water, when the butyrin remains as an oil which congeals at about 32° . It dissolves in all proportions of boiling alcohol, with this peculiarity, that the solution of 2 butyrin in 10 alcohol becomes turbid as it cools, whilst

* When the glands begin to secrete milk, it is at first very different from what it becomes afterwards, and has been termed *colostrum*; it is then more saline than perfect milk, and, in the cow, yellow, thick, and sometimes streaked with blood; it only contains traces of

butter, and coagulates, when heated, like a serous secretion; it gradually acquires the characters of perfect milk: it easily putrefies, without becoming sour.

† According to Chevreul, butter-milk contains *butyric acid*.

10 of butyrin in 12 alcohol remains clear. The alcoholic solution gradually becomes sour. Butyrin is easily saponifiable; its fat acids begin to congeal at 90° , but are not perfectly concrete till cooled to 62° .

When butyrin, freed from its associated stearin and elain, is saponified, it yields three distinct acids, termed, by Chevreul (*Recherches sur les Corps Gras*), *butyric*, *caproic*, and *capric* acid.

1. BUTYRIC ACID.—To obtain this acid, 5 parts of *butyrin* are saponified by 2 of hydrate of potassa; the resulting soap is dissolved in a large proportion of water, and decomposed by an excess of tartaric or of phosphoric acid; the liquid portion is then separated by filtration from the precipitated stearic and oleic acids, and subjected to distillation, when the three above-named acids, being volatile, pass over with the water. The distilled product is saturated by baryta, and gently evaporated to dryness. The residue consists of butyrate, caproate, and caprate of baryta; it is to be decomposed by concentrated phosphoric acid, which separates the three fat acids in the form of an oily liquid, and the portion which remains with the barytic salt may be abstracted by ether, and obtained either by distilling off the ether at 102° , or by its spontaneous evaporation. The oily mixture of the three acids is then agitated with its weight of water, which dissolves the butyric acid. The oily residue is then repeatedly washed with water, by which the caproic acid is dissolved, and the capric acid remains. The three acids being thus separated, should each be saturated by baryta, and the resulting salts crystallized. 100 parts of the butyrate of baryta are then decomposed by 63.36 parts of sulphuric acid diluted with its weight of water; the butyric acid, which separates, is then decanted off and distilled by gentle heat; it is then mixed with its weight of powdered chloride of calcium, and, after some days, again distilled by a gentle heat. The butyrate of baryta may also be decomposed by the addition of 1.32 parts of phosphoric acid, specific gravity = 1.12: the acid is then separated by decantation, and by agitation with ether.

Butyric acid is a limpid, colourless, inflammable liquid, resembling a volatile oil; it does not congeal at 15° ; it boils at a temperature somewhat above 212° , and volatilizes without decomposition. Its specific gravity is 0.9675 at 77° . It has a sour smell resembling that of rancid butter, and a pungent and slightly sweet taste; it leaves a white spot upon the tongue, and a greasy stain on paper, which gradually evaporates. It mixes in all proportions with water, but the presence of other acids diminishes its solubility. The density of a mixture of 2 parts of butyric acid and 1 of water is = 1.00287. Butyric acid apparently dissolves without decomposition in sulphuric and nitric acid. In combination with bases, it forms *butyrates*, which, when dry, are inodorous, but when moist smell strongly of butter. When decomposed by heat, they yield carburetted hydrogen and carbonic acid, and an aromatic oil which is not acid; the residue is carbonaceous. The neutral butyrates are soluble, but many of them lose a part of their acid during evaporation. Butyric acid is composed of

Carbon	8	48	62·34	Chevreul. 62·82
Hydrogen	5	5	6·49	7·01
Oxygen	3	24	31·17	30·17
Anhydrous butyric acid	1	77	100·00	100·00

In its ordinary state, the acid consists of 1 atom of anhydrous acid + 1 atom of water, which it throws off when it combines with oxide of lead; hence we have the formulæ

($8\text{ car} + 5\text{ h} + 3\text{ o}$) or *but'* = anhydrous butyric acid.

($8\text{ car} + 6\text{ h} + 4\text{ o}$) or (*but'* + *q*) = hydrated butyric acid.

BUTYRATE OF AMMONIA. ($A + \textit{but'}$).—Butyric acid, by absorbing ammoniacal gas, first forms a crystallizable compound, which, by further absorption, produces a liquid, and this afterwards concretes into a mass of acicular crystals.

BUTYRATE OF POTASSA ($P + \textit{but'}$) has a sweetish buttery taste, and is deliquescent and imperfectly crystallizable; 100 parts of water, at 60°, dissolve 125 of this salt, and the solution combines with a large additional proportion of acid.

BUTYRATE OF SODA ($S + \textit{but'}$) is less deliquescent than the potassa salt; in other respects its properties are similar.

BUTYRATE OF LIME ($C + \textit{but'}$) forms acicular crystals, of which 17 parts are soluble in 100 of water. This salt is less soluble in hot than in cold water, so that the cold solution concretes when heated; this effect is well observed in a tube, in which the hot and solid hydrated salt liquifies when plunged into cold water.

BUTYRATE OF BARYTA. ($B + \textit{but'}$).—This salt crystallizes in flat prisms, of a greasy lustre, and a buttery and alkaline taste; it restores the blue of reddened litmus. 100 parts of water at 50° dissolve 36 of this salt; it is a little soluble in anhydrous alcohol, and unchangeable in the air; in *vacuo* it loses 2·25 per cent. of water without becoming opaque.

BUTYRATE OF STRONTIA ($Str + \textit{but'}$) resembles the salt of baryta, but is less soluble.

BUTYRATE OF LEAD ($Pl + \textit{but'}$) forms small silky crystals; it easily loses acid during evaporation, and forms a tribasic salt.

BUTYRATE OF COPPER ($Cu + \textit{but'}$) forms transparent eight-sided prisms. Its solution at 212° deposits a blue powder, which soon becomes brown.

2. **CAPROIC ACID** is obtained by the decomposition of 100 parts of *caproate of baryta* by 29·63 of sulphuric acid, diluted with its weight of water; it is digested with chloride of calcium, and distilled. It is a very inflammable limpid oil, of an acrid acid flavour, leaving an impression of sweetness, and smelling like sour perspiration. Its specific gravity is 0·622 at 78°; it does not congeal at 15°. It boils above 212°, and

evaporates gradually in the air. Water at 42° scarcely dissolves 1·04 per cent. Anhydrous alcohol dissolves it in all proportions.

Caproic acid, in anhydrous combination, consists of

Carbon	12	72	68·57	Chevreul. 68·33
Hydrogen	9	9	8·57	9·00
Oxygen	3	24	22·86	22·67
Anhydrous caproic acid	1	105	100·00	100·00

The liquid acid consists of 1 atom of anhydrous acid + 1 atom of water ($105 + 9 = 114$), so that we have the formulæ

($^{12}\text{car} + ^9\text{h} + ^3\text{o}$) or *capro'* = anhydrous caproic acid.

($^{12}\text{car} + ^{10}\text{h} + ^4\text{o}$) or (*capro'* + *q*) = hydrated caproic acid.

CAPROATES.—These salts smell and taste like the acid; they exhale an aromatic odour when decomposed by heat. Their solubility is intermediate between that of the butyrates and caprates. *Caproate of potassa* forms a very soluble gelatinous compound, which becomes opaque when heated. *Caproate of lime* crystallizes in quadrilateral plates, soluble in twice their weight of water. *Caproate of baryta*, when crystallized at 65°, forms hexangular tables; at 85° its crystals are acicular. 100 parts of water at 50° dissolve 8 of this salt. It is fusible at a moderate heat.

3. CAPRIC ACID.—100 parts of the *caprate of baryta* are decomposed by 47·5 of sulphuric acid, diluted with its weight of water; or by 83·6 of vitrified phosphoric acid dissolved in 240 parts of water. The capric acid is distilled after having been digested upon chloride of calcium.

Capric acid forms small acicular crystals, which fuse at about 65°, at which temperature its specific gravity is 0·910. It may be distilled, without decomposition, at a little above 212°. Water at 65° dissolves scarcely a thousandth of its weight of capric acid, but alcohol dissolves it in all proportions. Its odour partakes of that of the goat.

Capric acid consists of

Carbon	18	108	74·0	Chevreul. 74·00
Hydrogen	14	14	9·6	9·75
Oxygen	3	24	16·4	16·25
Anhydrous capric acid	1	146	100·0	100·00

The crystallized acid includes 1 atom of water ($146 + 9 = 155$), hence the formulæ

($^{18}\text{car} + ^{14}\text{h} + ^3\text{o}$) or *cap'* = anhydrous capric acid.

($^{18}\text{car} + ^{15}\text{h} + ^4\text{o}$) or *cap'* + *q* = hydrated capric acid.

CAPRATES.—The humid caprates have the odour and taste of the acid; exposed to heat, they exhale an aromatic and goaty odour.

CAPRATE OF BARYTA requires for its solution 200 parts of water at 67°; it is fusible, and of a bitter alkaline taste.

It will be remarked that each of the three acids of saponified butyrin include 3 atoms of oxygen in their equivalents, so that in the neutral

butyrates, caproates, and caprates, the oxygen in the base is to that in the acid as 1 to 3.

CURD OF MILK. CASEUM. LACTALBUMEN.—This, which is the coagulable or albuminoid principle of milk, may be separated by adding dilute sulphuric acid to skimmed milk, which forms a white coagulum, or *sulphate of caseum*; this is washed to deprive it of whey, and mixed and digested with carbonate of lime or baryta; the acid is thus abstracted by the earthy base, and the free caseum dissolves in the water, so that it may be separated by filtration; this solution is yellowish, and somewhat viscid; during evaporation it smells like boiled milk, and becomes covered with similar films, which may be successively removed; when dry, the caseum is yellow, and soluble in water, and the solution is coagulated by acids, especially when warm; and when left to itself, it putrefies and smells like old cheese*. The transparent desiccated caseum becomes opaque in alcohol, in which it is sparingly soluble. (FROMHERZ and GUGERT, *Schweigger's Jour.*, L. 72.)

Caseum closely resembles albumen in regard to the action of the acids; the principal difference being, that it is precipitated by acetic acid; the precipitate is redissolved by excess of acid, but less easily than albumen or fibrin. The acid solutions of caseum are precipitated by ferrocyanuret of potassium. The alcoholic solutions of caseum are not precipitated by acids; and its acid compounds, which are insoluble in water, are soluble in alcohol. Caseum combines with the alkalis and alkaline earths, and its aqueous solution is precipitated by all those salts which throw down albumen, and also by tannin.

Caseum, like albumen, exists in the liquid and coagulated form; but its coagulation is not effected by boiling, but by the action of *rennet*, which is the inner coat of the calf's stomach after it has been washed in hot water. How this operates is unknown; but a similar coagulating power resides in the stomachs of most, if not all, animals. Berzelius put 1 part of the inner membrane of the calf's stomach, after having been well washed, into 1800 of skimmed milk, gradually heated up to 122°, and kept at that temperature till fully coagulated; he then took it out, washed, and dried it; it had only 6 per cent. in weight.

CHEESE is a mixture of coagulated caseum with more or less butter; its various qualities depend upon a variety of causes, partly connected with the properties of the milk employed, partly upon occasional additions to it, and peculiarities of manipulation; there are, however, two leading varieties dependent upon the absence and presence of butter; the former is a poor and comparatively hard and tasteless cheese, little prone to change, and when heated shrivels up like horn; the latter is rich, fusible, and when toasted, becomes soft and viscid, entering into a state of greasy semifusion. English cheese is frequently coloured by annotta, and often contains a preposterous quantity of salt, added partly to preserve it, and partly to increase its weight. The flavour and texture of cheese alters

* Braconnot conceives that dried caseum may be used as an article of food; and that with water, butter, and sugar, it might form a good substitute for milk in long voyages.

considerably by age; and if originally moist, it gradually passes into a peculiar state of putrefaction, the products of which have been examined by Braconnot (*Ann. de Ch. et Ph.*, xxxv. 161.) He found that curd covered with water, and kept at a temperature of about 75°, underwent complete putrefaction in about a month. The liquid was then filtered off, smelt putrid, and when evaporated to the thickness of honey, concreted into a granular mass, part of which was soluble in alcohol; the insoluble residue is what Proust (*Ann. de Ch. et Ph.*, x. 40,) termed *caseous oxide*; and the soluble portion, *caseate of ammonia*. Braconnot dissolved the caseous oxide in water, filtered through animal charcoal, and then obtained a colourless solution, which, by spontaneous evaporation, yielded a crystallized product: to this he gives the name of *aposepedin* (from *απο*, and *σηπεδων*, *product of putrefaction*).

Aposepedin is a friable crystalline substance, inodorous, slightly bitter, heavier than water, burns without residue, and when heated in a tube open at both ends, it rises in vapour, which deposits itself as a crystalline sublimate. Heated in a retort, this volatilization does not ensue, but it is decomposed, yielding concrete oil, and a liquid containing carbonate and hydrosulphuret of ammonia. It is very sparingly soluble in alcohol, and deposited from its boiling solution as it cools in the form of a light powder like magnesia; nitric acid decomposes it; hydrochloric acid dissolves it, and the evaporated solution concretes on cooling. Its aqueous solution yields a flocculent precipitate with infusion of galls, soluble in excess of the precipitant; subacetate of lead also throws down a white precipitate.

The supposed solution of *caseate of ammonia*, above-mentioned, contains, according to Braconnot, aposepedin, acetic acid, animal extractive, a resinous substance, several salts, and a peculiar oil, which is extremely pungent, and identical with that which is generated in old cheese, and gives to it its acrimony. Oleic and margaric acids, margarate of lime, and the acids of butyrin, are contained in the insoluble residue remaining upon the filter. The composition of aposepedin has not been ascertained; it probably contains a large proportion of nitrogen, and from its blackening effect upon silver, and the products of its destructive distillation, sulphur seems to be one of its elements.

The equivalent of caseum or lactalbumen cannot be determined, so that its atomic constitution must be hypothetical; it is given as follows by Gmelin, in reference to Gay Lussac's analysis:—

					Gay Lussac and Thenard.	
Carbon	7	.	.	42	.	60.87 . . 59.781
Hydrogen	5	.	.	5	.	7.25 . . 7.429
Oxygen	1	.	.	8	.	11.59 . . 11.409
Nitrogen	1	.	.	14	.	20.29 . . 21.381
Caseum	1			69		100.00 . . 100.000

The carbonaceous residue of caseum affords, when incinerated, about 6 per cent. of phosphate of lime, an ingredient in milk, which, as Berzelius remarks, forms an important feature in respect to the nourishment of young animals, who require it for the formation of bone.

WHEY. SUGAR OF MILK. LACTINE.—When the butter and curd of

milk are abstracted, there remains a pale yellowish opalescent fluid, termed *whey*, which, when evaporated, deposits a crystallized substance called *sugar of milk*, or *lactine*. Sometimes whey is evaporated to dryness, and the residue used as an article of food; in Switzerland, sugar of milk is an article of commerce; it forms crystallized cakes or masses of a prismatic and lamellar fracture; it is slightly sweet and gritty: its specific gravity = 1.543. It contains 12 per cent. of water, which may be evaporated by careful fusion, after which it concretes into an opaque white mass. Its water is also expelled by fusion with oxide of lead. It is slowly soluble, without forming a syrup, in 3 parts of hot and 6 of cold water, very sparingly soluble in alcohol, and insoluble in ether. It is not susceptible of vinous fermentation. It is convertible, like starch, into granular sugar, by boiling with a very dilute sulphuric acid. Nitric acid converts it into malic, oxalic, and *mucic* or *sacclactic acid* (p. 1071). Caustic potass and lime convert it into a brown bitter substance. When digested with oxide of lead and water, sugar of milk forms a soluble and an insoluble compound; the insoluble and anhydrous combination consists of 63.5 oxide + 36.5 sugar of milk; in this compound, the oxygen, according to Berzelius, in the oxide, is to that in the sugar, as 1 to 4, whence the following estimate of the equivalent and atomic composition of this organic product:—

				Berzelius.
Carbon	5	30	45.45	45.267
Hydrogen	4	4	6.06	6.385
Oxygen	4	32	48.49	48.348
Anhydrous sugar of milk	1	66	100.00	100.000

The *crystallized* sugar of milk consists of

				Berzelius.
Anhydrous sugar of milk	1	66	88	87.667
Water	1	9	12	12.333
Crystallized sugar of milk	1	75	100	100.000

Or,

				Berzelius.	Gay Lussac and Thenard.	Prout.
Carbon	5	30	40.00	39.474	38.825	40.00
Hydrogen	5	5	6.67	7.167	7.341	6.67
Oxygen	5	40	53.33	53.359	53.834	53.33
Crystallized sugar of milk }	1	75	100.00	100.000	100.000	100.00

Liebig (quoting Berzelius) give the following formulæ of sugar of milk, its hydrates, and combinations with oxide of lead.

Sugar of milk, crystallized	$(^{24}car + ^{19}h + ^{19}o) + 5(h + o)$
Ditto, dried at 248°	$(^{24}car + ^{19}h + ^{19}o) + 3(h + o)$
Ditto, dried at 300°, or anhydrous	$(^{24}car + ^{19}h + ^{19}o)$
Ditto, basic compound with oxide of lead	$(^{24}car + ^{19}h + ^{19}o) + 1(pl + o)$
Ditto, neutral ditto	$(^{24}car + ^{19}h + ^{19}o) + 5(pl + o)$

HUMAN MILK.—The statements respecting the composition of human milk are much at variance, arising probably in part from the difficulty of obtaining it in sufficient quantity for analysis, and partly from its muta-

bility in regard to the relative proportions of its component parts. L. Gmelin and Berzelius have each given the details of the experiments which have been made upon it. Its specific gravity appears to vary between 1·020 and 1·025, or a little higher: its solid contents, according to Meggenhofen, vary between 11 and 12·5 per cent., and its albumen or caseum is said to furnish soluble combinations with acids, so that it is not coagulated by them. Of fifteen samples, only three were coagulated by acetic and hydrochloric acids; but they were all coagulated by *rennet*: this is an important fact, as establishing the distinct action of rennet from that of acids. The following are the results of three of Meggenhofen's analyses:—

	I.	II.	III.
Butter, acids, and salts . . .	9·13 . . .	8·81 . . .	17·12
Sugar of milk and salts . . .	1·14 . . .	1·29 . . .	0·88
Curd coagulated by rennet . . .	2·41 . . .	1·47 . . .	2·88
Water	87·25 . . .	88·35 . . .	78·93

The extraordinary proportion of butyraceous matter in III., shows the uncertainty of composition in this secretion: indeed, in all the above cases the quantity of butter appears to have been excessive, for Payen's results, which in regard to the total amount of solid matter agree with Meggenhofen's, do not give an average of more than 5·2 per cent. of that ingredient.

ASSES' MILK has a specific gravity = 1·023 to 1·0355; it yields a light white butter, which soon grows rancid: the curd is more difficultly separable than from cows' milk, but the whey is clearer, and contains more sugar of milk. It contains 2·9 cream, 2·3 caseum, 4·5 sugar of milk (per cent.): and, according to Van Stiptrian Luisius and Bondt, it is susceptible of vinous fermentation.

MARES' MILK has a specific gravity = 1·034 to 1·045; it yields little cream, but a large proportion of sugar of milk; a vinous liquor is obtained by the fermentation of its whey, known in Tartary under the name of *koumiss*.

GOATS' MILK is of a specific gravity = 1·036; its goaty odour is stronger from dark than from white goats; it yields much cream and butter, and this, besides the usual acids, yields a peculiar one, called by Chevreul *hircic acid*, which gives it its characteristic odour: its caseum is also abundant, and the whey easily pressed out of it. It contains in the 100 parts, 4·03 butter, 4·52 caseum, 5·86 residue of the whey, 85·50 water (PAYEN), 7·5 cream, 4·56 butter, 9·12 caseum, 4·38 sugar of milk. (S. LUISIUS and BONDT.)

SHEEP'S MILK, of the specific gravity of 1·035 to 1·041, yields much cream, the butter of which is semifluid, and easily becomes rancid: the butter is difficultly separable from the curd, so that the cheese which it yields is rich and greasy. It affords 11·5 cream, 5·8 butter, 15·3 caseum, 4·2 milk-sugar per cent.

It has not been ascertained how far all milk is susceptible, under favourable circumstances, of vinous fermentation, nor whether any common sugar is present in the milk which undergoes that change; milk-

sugar and water with a ferment will not produce a vinous liquor: Scheele found that the addition of an ounce of brandy to a quart of milk caused it to undergo acetous fermentation, and that in a month it yielded good vinegar when poured off the curd, and contained no lactic acid. According to Liebig, when milk is exposed to a temperature between 95° and 104° , carbonic acid is given off, and alcohol formed, probably in consequence of the conversion of the lactine into grape sugar.

At temperatures above 55° , milk absorbs oxygen, and becomes sour; between 68° and 75° , this takes place in a few hours, and the milk then curdles when boiled; but Gay Lussac found that fresh milk heated every other day, or in summer every day, up to 212° , might be kept for months without spoiling. Milk, which has become sourish, may be recovered by heating it with a little carbonate of potassa or soda, sufficient to neutralize its acid. When milk grows sour, the lactic acid which is produced combines with the curd, and the combination may be decomposed (as stated in regard to the *sulphate of caseum*) by alkalis, or alkaline earths.

The influence of food upon the milk is well known by the varieties of taste, colour, and odour, which are so produced. From some of the *Euphorbia*, and from the *Gratiola officinalis*, it is said to acquire a laxative power. Madder, saffron, the flowers of *Ranunculi*, and many other colouring matters communicate to it their tints. The volatile oils of the *didynamia* affect its odour. Various medicines apparently affect the properties of the milk, as indicated by its effects upon the infant; and the influence of affections of the mind upon the secretion are often very obvious; these subjects, however, have as yet engaged but little of the attention of the chemist.

LACTIC ACID.—This acid, as its name imports, was originally discovered in *sour milk* (SCHEELÉ, *Opusc.*, ii. 101); it was then recognised by Berzelius, in many animal fluids, and afterwards by Braconnot, as a product, along with acetic acid, of the sour fermentation of rice-meal, wheat-paste, the juice of the beet-root, and other vegetable substances; he gave it the name of *Nanceic acid* (from Nancy, the place of his residence). It has also been termed *Zumic acid* (from ζυμη, *leaven*). It was supposed to be a compound of acetic acid with organic matter, but the error of that conclusion has been proved by Pelouze and Jules Gay Lussac. (*Ann. de Ch.*, lii. 410.) It has been found by Coriol combined with lime and magnesia, in the fermented infusion of *nux vomica*. (*Jour. de Phar.*, xix. 155, 373.)

Lactic acid may be obtained as follows:—Expose the expressed juice of beet-root to a temperature between 75° and 85° ; in some days fermentation comes on, and continues for about two months; when this has ceased, the juice is evaporated to the consistency of syrup, during which crystals of *mannite* separate: it is then treated by alcohol, which takes up lactic acid, and which may be to a certain extent purified by evaporation and solution of the residue in water; a portion of insoluble impurity remains: this aqueous solution of the impure lactic acid is then saturated by carbonate of zinc; the soluble lactate of zinc is separated by filtration, and crystallized; it is then redissolved in water, boiled with animal charcoal, and filtered whilst hot; on cooling, the *lactate of zinc* separates

in white crystals, which are washed with alcohol, decomposed by baryta, and the lactate of baryta, which is soluble, is decomposed by sulphuric acid. By a similar process lactic acid may be obtained from thoroughly sour milk. The aqueous solution of the acid may be concentrated in vacuo, and finally rendered quite pure, by solution in ether, which leaves a little flocculent matter.

Lactic acid is colourless, inodorous, very sour, of a syrupy consistence, and its specific gravity is 1·215; it attracts moisture from the air, and dissolves in all proportions in water and alcohol, and in smaller quantity in ether. It easily coagulates milk, and has a considerable solvent power over phosphate of lime, which induces Berzelius to regard it as the solvent of that salt in many animal fluids. Added to a strong solution of acetate of magnesia, it forms a granular precipitate of *lactate of magnesia*, and the odour of acetic acid is exhaled.

When lactic acid is cautiously heated, it first becomes more liquid, it then yields inflammable gases, acetic acid, and a white sublimate, which is *crystallized lactic acid*, and charcoal remains. These crystals, dried by pressure in bibulous paper and dissolved in alcohol, yield perfectly white rhomboidal tables, fusible at 225°, and volatile at 472°; this vapour again condenses in crystals, which, when dissolved in water, yield an acid exactly resembling the original: according to J. Gay Lussac and Pelouze, the crystallized acid is anhydrous, and consists of

Carbon	6	36	50·0
Hydrogen	4	4	5·6
Oxygen	4	32	44·4
<hr/>					
Anhydrous lactic acid	1		72		100·0

The lactic acid, as it exists in the neutral lactates in their driest state, and exclusive of water of crystallization, carries with it 1 atom of water, or of the elements of water, and is therefore, in them, represented by 72 + 9 or 81; its formula being ($6\text{ car} + 5\text{ h} + 5\text{ o}$).

The syrupy acid includes 2 atoms of water, so that in combining with bases it throws off 1 atom, and retains 1, whilst the crystallized acid, in similar cases, resumes an atom of water. No *anhydrous lactate* therefore has been obtained.

CHARACTERS OF THE LACTATES. — All these salts are soluble, and many of them are uncrystallizable. The *lactates of potassa* and of *soda* are deliquescent and soluble in alcohol; they yield crystalline masses by evaporation *in vacuo*. *Lactate of ammonia* is deliquescent and uncrystallizable. *Lactates of baryta*, and of *lime* yield gum-like masses; those of *alumina*, of *peroxide of iron*, and of *copper*, are uncrystallizable; *lactate of magnesia* is crystallizable, and *lactate of zinc* yields four-sided prisms, sparingly soluble in water and insoluble in alcohol; they contain 4 atoms of water. *Lactate of silver* forms white acicular crystals.

§ III. BILE. BILIARY CONCRETIONS.

THIS important secretion has been laboriously examined by several modern chemists of eminence, among whom we may especially enumerate Thenard (*Mémoires d'Arcueil*, i.), Berzelius (*Lehrbuch der Thier.*, and *Med. Chir. Trans.*, iii.), Tiedemann and Gmelin (*Über die Verdauung*, Essay on Digestion), and Frommherz and Gugert. (*Schweigger's Journal*, v. 1.) Their results, however, are so much at variance, that it is impossible to draw any general conclusions from them respecting the real nature and chemical components of the bile; these discrepancies seem partly to arise from the extreme facility with which chemical agents react upon this secretion, so that many of the supposed *educts* or component parts, which have been enumerated, are probably *products* of the different operations to which it has been submitted, or at all events, modifications of its true proximate elements: it has been therefore well observed by Berzelius, that our present chemical knowledge of the nature of bile can only be considered as a foundation for the more extended and satisfactory researches of future experimentalists. I shall here endeavour to select some of the least disputable and most important facts respecting the chemical properties of the bile, remarking at the outset, that the indications of reagents upon different specimens of bile are apt to vary, and that their action is often much modified by temperature, quantity, and the mode in which they are used.

There always appears to be mixed with bile a variable proportion of *mucus*, probably derived from the gall-bladder and its ducts, and not, therefore, a true component of the secretion: this gives the bile its viscidty, and often seems in some way to modify its other characters: in general, however (*ox-gall*), it is a green liquid, varying much in tint, of a peculiar odour, a bitter and nauseous taste, and a specific gravity fluctuating between 1.020 and 1.030. It does not coagulate when heated, and although it may possibly contain albumen, or something very like it, it is not immediately coagulated by alcohol or by dilute acids. The relative proportion of solid matter obtained by evaporation is between 8 and 10 per cent. By means of acetic acid, the mucus which is mixed with the bile may to a great extent be separated. In the *mammalia*, generally, the bile exhibits nearly the same characters; and in birds and fishes its components seem to be the same, but rather more dilute in the former, and more concentrated in the latter; it is always alkaline, from the presence of soda, apparently in the same state of combination as it exists in the serum of the blood. When bile is evaporated very carefully to about half its bulk, and alcohol added, (in the proportion of about 4 parts to 1 of the evaporated bile,) a coagulated matter is thrown down, which has some of the properties of albumen; yet neither solution of corrosive sublimate, nor of ferrocyanuret of potassium, which are such delicate tests of that proximate animal principle in other cases, enables us to detect it in the original bile. Chlorine first renders bile green, and then opaque and milky. Acetate of lead gives no precipitate, but subacetate of lead throws down a copious curdy substance. When alcohol is added to bile which has been evaporated nearly to dryness, it acquires,

when filtered off, a brownish-green colour and bitter taste: when evaporated, it leaves a residue which is almost totally soluble in water; and in this aqueous solution, dilute sulphuric acid slowly throws down a gray substance, which appears to be a compound of the acid and the bitter principle of the bile; when it has been washed with water (in which it is not soluble), it dissolves in alcohol, and if the sulphuric acid be then separated from it by carbonate of baryta and filtration, the filtered solution leaves on evaporation a green, transparent, bitter residue, which appears to be the characteristic principle of the bile, and which Berzelius calls *Gallenstoff*. As thus obtained, it is not quite free from foreign matters, and ether digested upon it takes up a little fatty matter: indeed, when bile, concentrated by evaporation, is agitated with ether, and the latter, after having separated upon the surface, is poured off and evaporated, it always leaves traces of a fatty substance, probably identical with *cholesterine*. The purified bitter residue, to which we have just adverted, is apparently the *picromel* of Thenard; it has a bitter, pungent, and sweetish taste, is inflammable, deliquescent, soluble in water and alcohol, but insoluble in ether; its solution is precipitated by many acids, (not by acetic or phosphoric,) and the precipitate is nearly insoluble in water, of a greenish colour, resinous appearance, and fusible at 212° . This precipitate (consisting of *picromel* combined with the acid used to throw it down) dissolves in alcohol, and is again thrown down by water: it dissolves in solution of acetate of potassa, the alkali of which combines with the acid of the precipitate, whilst the acetic acid unites to the *picromel* to form a soluble acetate. *Picromel* dissolves in weak alkaline solutions apparently without decomposition.

It will be seen from many of the above characters, that *picromel* (by which I mean Berzelius's *Gallenstoff*) may have been mistaken for albumen, and that it is not improbable that the only true albuminous part of the bile may be in that equivocal state which is often called *mucus*, and which is especially distinguished by being precipitable by acetic acid. Berzelius has suggested an analogy between *picromel* and the peculiar saccharine matter which is contained in liquorice-root; and in many respects their chemical properties are identical.

In the preceding statement, drawn principally from Berzelius, I have endeavoured to give the simplest view of the analysis of the bile; namely, the separation of its *muco-albumen* by acetic acid or alcohol, and of its *picromel*, by precipitation with acids and subsequent decomposition of the precipitate by carbonated baryta or alkali; its saline contents appear closely to resemble those of the serum of the blood; like which it has an alkaline reaction, due to soda. I have also selected such experiments, as, with me, have invariably succeeded: the following results, therefore, of the analysis of the bile, as given by Berzelius, will now be intelligible:—

Water	90.44
Picromel (<i>Gallenstoff</i>), including fat	8.00
Mucus of the gall-bladder	0.39
Extractive, common salt, and lactate of soda	0.74
Soda	0.41
Phosphate of soda and lime, and traces of a substance insoluble in alcohol	0.11

The details of the other analyses of the bile, as given by the authorities to which I have referred above, would be unintelligible if abridged, and are too voluminous to be inserted here; and moreover, I have generally failed in arriving at satisfactory conclusions, in my endeavours at a repetition of the various analytical operations which are described; I must therefore rest satisfied with giving, in a condensed form, a general statement of their results. According to Thenard, *human bile* contains, water 90·90; yellow bitter resin 3·73; yellow matter generally diffused through the bile (mucous and colouring-matter?) 0·18 to 0·90; albumen 3·82; soda, by which the resin is dissolved, 0·51; phosphate, sulphate, and chloride of sodium, phosphate of lime, and oxide of iron, 0·41. Tiedemann and Gmelin give the following as the components of human bile: 1. fat; 2. brown resin; 3. sweet principle of bile; 4. salivary matter; 5. mucus; 6. gall-brown (colouring-matter?); 7. oleic acid, salts, and minute quantities of other substances. Frommherz and Gugert (*Schweigger's Journal*, i. 8) have arrived at yet more complicated results: namely, 1. fat; 2. resin; 3. sweet principle; 4. osmazome; 5. salivary matter (*Speichelstoff*); 6. caseum; 7. mucus; 8. margaric and other fatty acids, with phosphate and sulphate of soda and potassa, chloride of sodium; and carbonate, phosphate, and sulphate of lime. The above and other chemists have published analyses of bile, taken after death in various diseases, but they present nothing very important. Tiedemann and Gmelin's elaborate analysis of *ox-gall* deserves the perusal of all chemists concerned in such inquiries: it contains, according to L. Gmelin, (*Handbuch der Theor. Chem.*, ii. 1012; Frankfurt, 1829,) a substance not to be found in any other bile, and which he has called *Taurin* or *Gallen-asparagin*: it may be obtained as follows:—Add hydrochloric acid to ox-gall, and filter; after a few days a fatty matter appears, which is separated by filtration: the filtered liquid is evaporated to a small bulk, when it separates into two parts—a resinous mass, and a sour fluid: the latter, upon further evaporation, yields more resinous matter, and at length crystals of common salt and taurin, which are to be separated, and the latter purified a second time by crystallization. Taurin, when purified, is in prismatic crystals, neither acid nor alkaline, not altered by exposure to air, inodorous, of a peculiar taste: soluble in about 15 parts of cold water, and nearly insoluble in absolute alcohol: it is fusible, and not decomposed by nitric acid.

More recently the bile has been examined by M. Demarçay (*Ann. de Ch. et Ph.*, lxxvii. 177), who regards it as a soap with a base of soda: that is, a combination of a peculiar fatty acid with soda, to which he has given the name of *choleic acid*.

BILIARY CALCULI, OR GALL-STONES.—These concretions have been especially examined by Gren, Thenard, Fourcroy, and, as to the fatty matter which they contain, by Chevreul. (*Ann. de Chim.*, xcv. 5.) Human gall-stones are, for the most part, composed of a crystalline aggregate of a species of adipocere, or as it has been termed by Chevreul, *cholesterine* (from *χολη*, *bile*, and *στερεος*, *solid*), with more or less colouring-matter, muco-albumen, and inspissated bile; they are accordingly of various colours and textures, but generally brittle and friable.

Those which are chiefly cholesterine, or as it should more properly be termed *cholestearine*, are white and crystalline, and lighter than water; the others are more tough, coloured, and dense; their specific gravities, therefore, vary from 0.803 to 1.06. Their chemical examination may be conducted as follows: They may be powdered, and digested in water to separate the inspissated bile: then boiled in alcohol, and the solution filtered whilst hot; as it cools it deposits the cholesterine, and often retains common fat and its acids in solution. The portion which resists the action of alcohol may be digested in a weak solution of caustic potassa, which takes up colouring matter and muco-albumen: the solution, supersaturated by acetic acid, deposits these, and the colouring matter may afterwards be removed by alcohol. Any common albumen may be detected by ferrocyanuret of potassium added to the acetic solution.

Cholesterine separates in white pearly scales from its hot alcoholic or ethereal solution during cooling; it fuses at about 280° , and when heated to about 400° , it sublimes: in the open air it burns like wax. Its ultimate components per cent. are 85 carbon, 12 hydrogen, 3 oxygen. It is the most carbonaceous of all the varieties of fat.

The *gall-stones of the ox* frequently consist chiefly of the yellow colouring-matter of the bile, which is occasionally used by painters, on account of its brightness and durability: it is insoluble in water and alcohol, but readily soluble in weak solution of potash, from which it is thrown down in green flocks by hydrochloric acid: nitric acid, cautiously dropped into a solution of this colouring-matter, gives it various shades of green, blue, and red. A *gall-stone from a sow* yielded cholesterine 6.0, resin 45, soda with resin 3.6, mucus, colouring matter, phosphate of lime, and oxide of iron, 45.4. (LASSAIGNE.)

§ IV. SALIVA. PANCREATIC JUICE. GASTRIC JUICE. LYPH. MUCUS. PUS.

SALIVA has been examined by Berzelius, and more in detail by Tiedemann and Gmelin. (*Ueber die Verdauung.*) The principal use of this secretion appears to be to attenuate, and mix with the food during mastication; it is consequently secreted in great abundance during a meal; at other times, only in such quantity as to lubricate the mouth and parts adjacent.

Human saliva is transparent, viscid, and contains an animal matter, frequently termed *mucus*, but its peculiarities have been pointed out by Berzelius, who designates it *salivary matter* (*Speichelsstoff*). Under the term *mucilaginous extractive*, a similar principle has been found in other animal fluids. The specific gravity of human saliva is 1.0043. It is generally slightly alkaline; sometimes neutral; and in some diseases (intermittent fever and abscess) sour; nitric acid separates from it transparent films. The salts of lead, tin, copper, and mercury, and infusion of galls, yield with it a dense white coagulum; it reddens a dilute solution of perchloride of iron. It loses from 99.1 to 98.81 per cent. by evaporation, and leaves a residue = 0.9 to 1.19. The dry residue contains fatty matter, with traces of phosphorus, osmazome, sulphocyanate, hydro-

chlorate, and acetate of potassa, (with a little soda,) 31·25. It affords to hot alcohol albuminous matter (caseum?) with a trace of sulphate of potassa, 1·25; salivary matter, with alkaline phosphates, and traces of sulphates and chlorides, 20·00; mucus, with carbonate and phosphate of lime, 40·00 (loss 7·5). By incineration, the dry residue of saliva yields 21·9 per cent. of ash, composed of 17·8 carbonate, phosphate, hydrochlorate, and a little sulphate of potassa (with traces of soda), and 4·5 phosphate of lime, with a little carbonate of lime and magnesia. (GMELIN.) According to Berzelius, the components of saliva are, salivary matter 0·29, mucus 0·14, osmazome with lactate of soda 0·09, soda 0·02, chloride of potassium and chloride of sodium 0·17, water 99·29. By transmitting a current of electricity through saliva I obtained indications of albumen, resembling those with other albuminous fluids. (*Phil. Trans.*, 1809.)

In the saliva of a person suffering under diseased lungs, whose perspiration smelt sour, and whose gastric juice contained much acetic acid, whilst the urine was highly alkaline, Dr. Prout found free acetic acid. (*Phil. Mag. and Ann.*, iv. 122.) During mercurial salivation, the specific gravity of the saliva was 1·0038, and contained albuminous flakes = 0·257 mucus 0·367, chloride of sodium 0·090, water 99·286. (THOMSON, *Ann.*, vi. 397.) In a similar case, in which the saliva amounted to two quarts daily, Dr. Bostock found it of a pale yellow colour and opaque; it deposited, in the course of twenty-four hours, viscid films, and became transparent; it became turbid at 212°, and with hydrochloric acid and corrosive sublimate it gave an albuminous precipitate: it left, on evaporation, 2 per cent. of dry residue. (*Med. Chir. Trans.*, xiii. 73.)

The saliva of the dog and of the sheep have been analyzed by Gmelin, and of the horse, by Lassaigne. (*Ann. de Ch. et Ph.*, xix. 176.) The saliva of the sheep contained so much carbonate of soda as to effervesce with acids, and also sulphocyanuret of potassium. Its solid matter amounted to 1·2 per cent. That of the dog left 2·51 per cent. of solid matter, but yielded only very slight traces of sulphocyanogen. The saliva of the horse afforded 3·5 per cent. of solid residue, and deposited carbonate and phosphate of lime.

SALIVARY CONCRETIONS.—These are sometimes found in the salivary ducts and glands; they have been repeatedly analyzed, and consist of phosphate of lime, carbonate of lime, &c., and albuminous matter. A calculus from the salivary duct of a woman sixty years of age, was white, friable, specific gravity = 2·30. It contained animal matter 25, phosphate of lime 55, carbonate of lime 15, carbonate of magnesia 1, oxide of iron 2? loss 2. (BOSSON.) A calculus from the salivary gland of an ass, contained 91·6 carbonate of lime, 4·8 phosphate of lime, and 3·6 animal matter. (CAVENTOU.) A salivary stone from a horse consisted of, 85·52 carbonate of lime, 7·56 carbonate of magnesia, 4·40 phosphate of lime, and 2·48 of animal matter. (HENRY, jun.)

TARTAR OF THE TEETH.—This term is applied to a deposit formed upon those parts of the teeth which are protected from the cleansing influence of the tongue, and is most abundant in the mouths of persons who speak much, and keep the mouth open, so as to allow of the evapo-

ration of the saliva. It consists of animal matter and earthy phosphates. Berzelius obtained from 100 parts of this substance; salivary matter 1·0, mucus 12·5, earthy phosphates 79·0, animal matter soluble in hydrochloric acid 7·5. According to Vauquelin and Laugier it contains 0·13 insoluble mucus, 0·66 phosphate of lime with a trace of magnesia, 0·09 carbonate of lime, 0·05 soluble animal matter, 0·07 water.

PANCREATIC JUICE.—This secretion, from a dog, contains, according to Gmelin, albumen, and a substance like curd, a small quantity of mucus and osmazome, (salivary matter?) and a free acid. Its salts resemble those of saliva, excepting sulphocyanates. It afforded 91·72 per cent. of water. That from the sheep contained, 1·51 substances soluble in alcohol, 0·28 soluble in water, 2·24 coagulated albumen, 96·35 water. The supposed analogy between saliva and the secretion of the pancreas seems, therefore, to be disproved.

GASTRIC JUICE.—The extraordinary solvent powers of this secretion, and its property of coagulating milk (and other albuminous liquids?) have been long known, but its chemical nature does not satisfactorily explain these properties. We are indebted to Dr. Prout for the curious discovery of the presence of hydrochloric acid in this secretion, (*Phil. Trans.*, 1824;) he found it together with acetic acid (lactic acid?) in the gastric juice of the rabbit, hare, horse, calf, and dog, and in the sour matter thrown up by persons suffering from indigestion, a fact also confirmed by Mr. Children. According to Tiedemann and Gmelin, any foreign matter in the stomach excites this acid secretion, but especially stimulating food. The other properties of gastric juice will be mentioned when considering the phenomena of digestion.

LYMPH.—This term is applied to the fluid which lubricates the different cavities of the body, and which moistens its cellular textures; it sometimes collects in morbid quantity, as in *dropsies*, and is found in the thoracic duct of an animal that has been kept for twenty-four hours without food. The liquid of vesications seems, chemically speaking, closely to resemble it. It is colourless, transparent, miscible in all proportions with water, does not affect vegetable blues, and is not coagulated by acids or by alcohol. When evaporated to dryness it yields slight traces of albuminous matter*.

Its composition, however, in dropsical cases, is liable to much variation, depending probably upon the cause of its accumulation, and the manner

* The human *liquor amnii* is ammoniacal and albuminous; it yields copious precipitates with corrosive sublimate and infusion of galls. It is also said to contain benzoic acid and urea. Soda, chloride of sodium, and phosphate and carbonate of lime, are also contained in the amniotic fluid; and Dr. Prout found traces of sugar of milk in it. (*Ann. of Phil.*, v. 417.) The solid contents amount to between 2 and 3 per cent. The acid described by Buniva and Vauquelin, as peculiar to the *liquor*

amnii of the cow, and termed *amniotic acid*, was found by Dzondi to belong to the liquor of allantois, or to the urine of the fœtus. The *allantoic acid* is obtained by evaporating the allantoic liquid of the fetal calf: it forms white acicular crystals, sparingly soluble in water, but yielding soluble salts with the alkalis. It has been produced artificially by Liebig, by the action of peroxide of lead on uric acid. See page 1377.

in which it has been thrown out. When this has been a very gradual process its characters are those of common lymph; but when rapid, or attended by inflammatory action, it is more abundant in albumen, and sometimes approaches *serum* in its characters and composition—hence dropsical fluids are often very dissimilarly constituted, as far, at least, as regards quantitative composition.

MUCUS.—All animal fluids of a viscid or glairy consistence, and not partaking of the decided characters of albumen, were formerly classed under this term, till Mr. Hatchett, in his valuable essays on animal substances, and especially in his observations on the component parts of membrane, showed the necessity of assigning to it a more definite meaning. Dr. Bostock includes, under the term *mucus*, animal substances which are soluble in hot and cold water; not precipitated by tannin or corrosive sublimate; not gelatinizable; but which are thrown down by subacetate of lead. Fourcroy and Vauquelin improperly compare it to gum. Berzelius remarks, that if the term *mucus* be restricted to the secretion from what are termed *mucous membranes*, it will include a variety of dissimilar products, and in the paper already quoted, I have shown that the characters generally ascribed to *mucus*, are in some cases derived from peculiar forms or combinations of albumen.

The secretion which is most appropriately termed *mucus*, is that from the nasal membrane; its properties are amply given by Berzelius. It appears when first secreted to be thin and aqueous, but, subject from its situation to the constant action of air, and to evaporation, it gradually thickens. It contains *mucus* (a peculiar animal principle) 5·33, extractive matter soluble in alcohol and an alkaline lactate 0·30, chlorides of potassium and sodium 0·56, extractive matter soluble in water only with traces of albumen and a phosphate 0·35, soda combined with the *mucus* 0·09, water 93·37. Of these components the *mucus* is the only one which is peculiar to this secretion; its properties are defined by Berzelius as follows: it swells and acquires apparent fluidity in water, without being actually dissolved, but gives a ropiness to it when present to a less amount than 1 per cent. With pure water of the temperature of 95° this appearance ensues in a few hours, but if the apparent solution be filtered, the *mucus* remains upon the paper and gradually thickens; it may be repeatedly dried and moistened without material change of properties; it, however, becomes less transparent, yellow, and at length has a purulent appearance. When boiled in water it does not harden and shrink, but becomes tough, and on cooling is found to retain its former characters. When dried, it is yellow and translucent; subjected to destructive distillation, it yields carbonate of ammonia and empyreumatic oil, and phosphate and carbonate of lime, and a trace of carbonate of soda, are found in the residuary ash. It is soluble in dilute sulphuric acid, and is blackened and decomposed by the concentrated acid. Dilute nitric acid coagulates, and tinges it superficially yellow, after which it swells and becomes viscid as at first: when digested in the acid it is entirely dissolved. Acetic acid coagulates, but does not dissolve it; it, however, acquires a trace of albumen, and consequently becomes cloudy on the addition of ferrocyanuret of potassium. Caustic potassa first

renders it more viscid, and then dissolves it. Infusion of galls thickens and coagulates it in all its states.

PUS.—This, and the term *purulent matter*, is applied to the secretion of inflamed and ulcerated surfaces, and its characters are very different according to the circumstances under which it is secreted. When it indicates a healing sore, it has been called *healthy pus*, and has the following properties. It has the consistency of cream, a yellowish colour, and exhibits, under the microscope, the appearance of globules diffused through a fluid. (HOME, *On Ulcers*, 2nd edit., p. 13.) Its specific gravity is about 1.030. It does not affect vegetable colours till it has been some time exposed to air, when it becomes slightly sour; it does not easily mix with water, alcohol, or dilute acids. (PEARSON, *On Pus*, *Nicholson's Journal*, xxx.) The composition of pus has not been accurately determined, and there is no accurate test by which it can be satisfactorily distinguished from albuminous and mucous secretions, when, as is almost always the case, it is more or less mixed with those animal fluids.

TEARS contain a small portion of albumen combined with soda, hydrochlorate of soda, and water. There are also small portions of other salts.

HUMOURS OF THE EYE.—The *aqueous* and *vitreous humours* are composed of water holding a minute quantity of albumen and saline matter in solution; the *crystalline lens* also contains more than half its weight of water, the remainder being an albuminous substance with traces of hydrochlorates.

SYNOVIA is the fluid which lubricates the surfaces of joints. It contains, according to Mr. HATCHETT (*Phil. Trans.*, 1799), a small portion of phosphate of lime, and of phosphate of soda and ammonia; the animal principle appeared to be albumen.

In *Oysters*, in the vertebral fluid of the *Squalus maximus*, and in *frog-spawn*, are contained modifications of *mucus*; that of frog-spawn is very remarkable from the extent to which it swells up in water, forming a very bulky and transparent jelly, so that a piece not larger than a pea of the recently-emitted gelatinous matter that envelops the ova of the frog, will gradually absorb and gelatinize 8 or 10 ounces of water.

§ V. URINE. UREA. URIC ACID. URINARY CALCULI.

URINE.—This secretion carries off several substances from the blood, which may be termed excrementitious, and which would be injurious if retained; these substances are, for the most part, abundant in nitrogen. The *quantity* of urine which is formed, or secreted, in the ordinary and healthy state of the system, is very variable, depending upon the quantity of liquids taken into the stomach, the extent of perspiration, and apparently in many cases, upon the dry or humid state of the atmosphere, a cause by which the abstraction of moisture by the skin is greatly modified. Between 30 and 40 ounces may, perhaps, be considered as the average quantity of the urine voided by a healthy person, living upon ordinary diet, in the course of each 24 hours.

But the *quality* of the urine is no less variable than its quantity, so that its density is perpetually varying; sometimes its specific gravity scarcely exceeds that of water; at others, it rises to 1·030, or even in some diseased states, to 1·040; that which is voided in the morning by a person who has eaten and drunk moderately of usual diet is usually a little on one side or other of 1·020.

Recent healthy urine always has more or less of an acid reaction upon tests; after it has stood in an open vessel for a few hours, this acidity gradually becomes less apparent, and it generally deposits a little mucus, containing traces of acid urate of ammonia. It is extremely prone to other and more complicated changes, and in warm weather it begins in the course of a few hours to acquire new properties: it becomes alkaline, acquires a highly-disagreeable odour, and lets fall a whitish sediment, consisting chiefly of ammonio-magnesian phosphate, and phosphate of lime; it afterwards smells ammoniacal, and is found to hold carbonate of ammonia in solution. Similar changes may be effected by continued boiling; they are chiefly referable to the decomposition of the characteristic ingredient of the urine, namely *urea*, a substance which is easily resolved into carbonate of ammonia.

The substances always found in healthy urine are the following:—

- | | |
|---|---------------------------|
| 1. Water. | 6. Phosphate of ammonia. |
| 2. Carbonic acid. | 7. Phosphate of soda. |
| 3. Phosphoric acid, or super-phosphate of lime. | 8. Phosphate of magnesia. |
| 4. Uric acid, or superurate of ammonia. | 9. Common salt. |
| 5. Phosphate of lime. | 10. Sulphate of soda. |
| | 11. Albumen. |
| | 12. Urea. |

To which may probably be added,

- | | |
|------------------------------------|-----------------------------------|
| 13. Fluoric acid. | 19. Fluat of lime. |
| 14. Benzoic acid. | 20. Hydrochlorate of ammonia. |
| 15. Acetic or lactic acid. | 21. Sulphur. |
| 16. Gelatine. | 22. Silica. |
| 17. Lactate or acetate of ammonia. | 23. Mucus. |
| 18. Sulphate of potassa. | 24. Colouring and odorous matter. |

To this extensive list may be added a great variety of occasional or accidental ingredients derived from particular kinds of food or medicine, and which pass off by the kidneys; and lastly, certain substances which are apparently products of disease, such as oxalic acid or oxalate of lime, carbonate of lime, cystic oxide, sugar, and nitric acid.

From this complicated character of the urine, from the variations to which the quantity and quality of its components are liable, and from the facility with which it passes into a state of decomposition, and is modified by heat and other chemical agents, it becomes extremely difficult to give even an average statement of the relative proportions of its usual ingredients; as a specimen, however, of such an attempt, I quote the following from Berzelius:—

Water	933·00
Urea	30·10
Sulphate of potassa	3·71
Sulphate of soda	3·16
Phosphate of soda	2·94

Chloride of sodium	4.45
Phosphate of ammonia	1.65
Hydrochlorate of ammonia	1.50
Free lactic acid	} 17.14
Lactate of ammonia	
Animal matter soluble in alcohol	
Urea not separable from the preceding	
Earthy phosphates, with a trace of fluete of lime	1.00
Uric acid	1.00
Mucus of the bladder	0.32
Silica	0.03
<hr/>	
1000.00	

A question has arisen as to the existence of *free acid* in the urine, as stated by Berzelius and others; Dr. Prout regards the acidity of the urine as the result of the presence of acid or super-salts, and especially of superphosphate of lime and superurate of ammonia. Dr. Turner observes, "That a very strong argument, which to him appears conclusive in favour of this view, is, that on adding hydrochloric acid to recent urine, minute crystals of uric acid are gradually deposited, as always happens when this acid subsides slowly from a state of solution, but on the contrary, if no free acid is added, an amorphous sediment, which Dr. Prout regards as superurate of ammonia, is obtained." We know, however, too little of the mutual actions of the complex ingredients of the urine, to sanction this opinion; carbonic acid is certainly, sometimes at least, present in a free state, and whether other acids may or may not exist free, and therefore in variable quantities in reference to the bases, is, I think, a question which cannot at present be determined. At all events, the presence of free acid in certain morbid states of the urine, cannot admit of a doubt. One important consequence of the acid state of the urine appears to be the retention of certain difficultly-soluble salts in permanent solution; for whenever the urine is neutralized by an alkali, these are more or less precipitated; an effect of this kind not unfrequently takes place in the body, as we see from the turbid state in which the urine is voided after sufficient doses of the caustic or carbonated alkalis, or of magnesia.

The properties and composition of the ordinary acids, bases, and salts of the urine, are already before the reader; the chemical history of *urea*, and of *uric acid*, bodies which peculiarly characterize urine, remain to be noticed.

UREA is the principle which confers upon urine its chief peculiarities. It may be obtained by slowly evaporating urine to the consistency of syrup; on cooling it concretes into a saline mass, which, by digestion in alcohol, furnishes urea. By carefully distilling off the alcohol, the urea remains in the form of a brown crystallized mass, which, by purification, furnishes colourless prismatic crystals. Or, concentrated nitric acid may be added to the brown urea, which forms with it a crystallized mass, which, after having been washed with a little cold water, is to be dried by pressure in blotting-paper. The *nitrate of urea* thus formed is to be decomposed by neutralizing it with a strong solution of carbonate of potassa, and the solution set aside, after having been duly evaporated, to

separate the nitre by crystallization. The mother-liquor, which is an impure solution of urea, is mixed with animal charcoal into a paste, which, after some hours, is lixiviated with cold water; the urea is dissolved, and the solution evaporated to dryness, at a low temperature. The residue is then digested in pure alcohol, which deposits crystals of urea on cooling. (PROUT, *Med. Chir. Trans.*, viii.)

The form of these crystals is a four-sided prism; they are transparent, colourless, of a peculiar and cooling taste, a faint, but not urinous odour, neutral, slightly deliquescent, and of a specific gravity = 1.35. Urea dissolves in about its weight of water at 60°, and in 5 parts of cold, and 1 of boiling alcohol. This solution is not prone to decomposition unless other ingredients of the urine be present; it is then, by continued ebullition, almost entirely resolved into carbonate of ammonia. Urea is also decomposed by the caustic alkalis and alkaline earths. It fuses at 250°, and at a somewhat higher temperature it is resolved into carbonate of ammonia and *cyanuric acid*. Although not alkaline, urea forms definite and crystallizable compounds with nitric and oxalic acids; and this property forms a good characteristic test of the presence of urea.

Urea consists of

Carbon	2	12	20.00	Prout.	19.975
Hydrogen	4	4	6.67		6.650
Oxygen	2	16	26.66		26.650
Nitrogen	2	28	46.67		46.650
Urea	1	60	100.00		99.925

By referring to the composition of cyanic acid, ammonia, and water, it will be apparent that an atom of urea = ($2\text{car} + 4\text{h} + 2\text{o} + 2\text{n}$) is equivalent to, and contains the elements of an atom of *hydrated cyanate of ammonia* = ($\text{A} + \text{cy}' + \text{q}$) or $(\text{n} + 3\text{h}) + (\text{n} + 2\text{car} + \text{o}) + (\text{h} + \text{o})$. Hence the production of urea by the mutual action of ammonia, cyanic acid, and water, as by decomposing cyanate of silver by hydrochlorate of ammonia, or cyanate of lead by a solution of ammonia; in the latter case, oxide of lead falls, and it might be presumed that cyanate of ammonia would be formed, but on evaporating the filtered liquor, quadrangular crystals are obtained, which yield no ammonia by the action of potassa, nor do they precipitate solutions of lead or of silver, as is the case with the soluble cyanates; in this case, therefore, *urea is formed artificially*, and it presents a curious case of isomerism. Dumas regards urea as an ammidé of oxide of carbon, or as $(\text{n} + 2\text{h}) + (\text{c} + \text{o})$.

URIC ACID. LITHIC ACID. ($10\text{car} + 4\text{h} + 6\text{o} + 4\text{n}$.)—This acid has been mentioned as one of those which are found in human urine; it often constitutes urinary concretions; it is found in the urine of birds of prey and of those which feed on fish and animal matter. The substance called *guano*, which is the decomposed excrement of aquatic birds, and which abounds in many of the small islands of the South Sea, and is used as a manure, is also chiefly composed of urate of ammonia. It is also found in the excrement of the parrot and some other birds which feed upon vegetables, and also in cantharides and in the excrement of silk-

worms. The excrement of large snakes, especially that of the *boa constrictor*, consists of white nodules containing little else than urate of ammonia.

Uric acid is generally obtained from the excrement of the *boa* by dissolving it in solution of caustic potassa, and dropping the hot solution into dilute sulphuric, hydrochloric, or acetic acid; the precipitate, when thoroughlyedulcorated and dried, is pure *uric acid*. It is a white, crystalline, tasteless, inodorous powder, nearly insoluble in water, requiring, according to Prout, 10,000 parts of water at 60° for solution; it is insoluble in alcohol and in ether, it feebly reddens litmus, and combines with bases. When mixed with nitric acid, and evaporated carefully to dryness, a crimson or scarlet compound remains, which becomes bright purple when moistened with ammonia; this is a ready and characteristic test of uric acid: the substance called by Brugnatelli *Erythric acid*, and by Prout *Purpuric acid*, the *Alloxan* of Wöhler and Liebig, is one of the products of this decomposition, and is noticed further on. Uric acid is decomposed by chlorine; when *dry*, and heated in the gas, cyanic and hydrochloric acids are formed; if *moist*, cyanic and carbonic acids, while hydrochlorate and carbonate of ammonia remain in solution. Fused with hydrate of potassa, uric acid yields carbonic acid, cyanuret of potassium, and cyanate of potassa. When distilled *per se* it yields carbonate and hydrocyanate of ammonia, and a sublimate of *pyro-uric* or *cyanuric acid*.

According to Liebig the ultimate elements of uric acid (which is anhydrous), are

				Liebig.			Prout.		
Carbon	10	.	60	.	35·7	.	36·11	.	39·875
Hydrogen	4	.	4	.	2·4	.	2·34	.	2·225
Oxygen	6	.	48	.	28·6	.	28·19	.	26·775
Nitrogen	4	.	56	.	33·3	.	33·36	.	31·125
Uric acid	1		168		100·0		100·00		100·000

URATE OF AMMONIA. ($A + ur'$).—The neutral urate of ammonia is soluble, according to Prout, in 480 parts of water at 60°, and the solution yields a precipitate of uric acid on the addition of the other acids: triturated with solution of potassa it evolves ammonia; this salt occurs in the urine, and in urinary calculi; but according to Coindet the excrement of snakes and birds contains a *binurate of ammonia*.

URATE OF POTASSA ($P + ur'$) is formed by digesting uric acid, or urate of ammonia, in a hot solution of caustic potassa, till it is neutral; on cooling, the salt is deposited in granular crystals, or by slow evaporation, in crystalline scales soluble in about 500 parts of cold water; but it is much more soluble in boiling water, especially if there be excess of alkali; in this case, however, the neutral urate is also deposited. When urate of potassa is dissolved in solution of potassa, carbonic acid throws it down in the form of a bulky gelatinous precipitate; it is also precipitated by carbonate of ammonia. When the dry salt is exposed to air it absorbs carbonic acid, and carbonate and binurate of potassa are formed. Digested in a solution of carbonate of potassa, uric acid forms a transparent gelatinous hydrated urate of potassa, and the solution contains bicarbonate of potassa. When subjected to destructive distillation, urate of potassa

leaves cyanuret of potassium. When uric acid is fused with caustic potassa, ammonia is evolved, and oxalate of potassa formed.

URATE OF SODA. ($S + ur'$).—The mutual action of uric acid and solution of caustic soda, resembles that of potassa. This salt constitutes the white concretions which form in the joints of gouty persons, and which are called *chalk stones*. (WOLLASTON.)

URATE OF LIME. ($C + ur'$).—The solution of uric acid in lime water yields pulverulent or minute acicular crystals of this salt. The addition of hydrochloric acid to the solution, throws down a *binurate of lime*.

URATE OF BARYTA ($B + ur'$) may be formed by digesting uric acid in baryta water; or by adding urate of potassa to soluble barytic salts. *Urate of strontia* and *urate of magnesia* may also be obtained by double decomposition; according to Wetzlar, when uric acid is boiled in water with the earthy carbonates, carbonic acid is expelled, and urates of the bases are formed. Many of the metallic urates may be formed by double decomposition: the *urate of mercury* so obtained yields, when heated, carbonic and hydrocyanic acid, and much cyanic acid, but no free cyanogen. (WÖHLER.)

PURPURIC ACID.—This compound was first examined by Dr. Prout. (*Phil. Trans.*, 1818.) Its name indicates the colour of its compounds, for, though colourless itself, it produces purple salts. It may be obtained as follows. (TURNER'S *Elements*.) "Let 200 grains of uric acid prepared from the urine of the *Boa Constrictor* be dissolved in 800 grains of pure nitric acid, diluted with an equal weight of water, the uric acid being added gradually, in order that the heat may not be excessive. Effervescence ensues after each addition, nitrous acid fumes appear, heat is evolved, and a colourless solution is formed, which, on standing in a cool place for some hours, yields colourless crystals which have the outline of an oblique rhomboidal prism. By gentle evaporation, an additional quantity may be obtained. They contain nitric and purpuric acid, and ammonia; should be dissolved in water, and be exactly neutralized by pure ammonia, and the liquid then digested in a solution of potassa until the ammonia is wholly expelled: on pouring this solution into dilute sulphuric acid, purpuric acid is set free, which being insoluble in water, subsides as a granular powder, of a white colour if pure, but commonly of a yellowish-white tint." Dr. Turner observes "that considerable uncertainty prevails as to the nature of purpuric acid. Vauquelin denied that its salts have a purple colour, attributing that tint to some impurity; and Lassaigne is inclined to the same opinion (*Ann. de Ch. et Ph.*, xxii. 334); but from the intense colour given even by a very minute quantity of purpuric acid, the opinion of Dr. Prout appears to be the more probable. The composition of the acid is likewise unsettled, for Prout has expressed a doubt of the accuracy of the analysis which he formerly published."

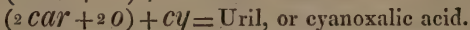
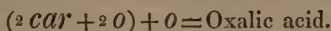
Dr. Prout's analysis represented purpuric acid as ($2car + 2h + 2o + n$), its equivalent being 44. This acid reddens in the air, either from the formation or absorption of ammonia: it reddens when heated, and

burns away without any peculiar odour. It is decomposed by concentrated nitric acid and by chlorine. It requires more than 10,000 parts of water for solution, and is soluble (without decomposition) in sulphuric acid. It expels carbonic acid from the carbonated alkalis, and forms red salts, most of which contain 2 atoms of acid to 1 of base.

PURPURATE OF AMMONIA forms four-sided prisms of a red colour and sweetish taste, soluble in 1500 of cold and in much less of hot water, and insoluble in alcohol and ether: the aqueous solution is carmine-red. *Purpurate of potassa* is dark-brownish purple, and much more soluble in water than purpurate of ammonia. *Purpurate of soda* requires 3000 parts of water at 60° for solution. *Purpurate of baryta* is thrown down in the form of a dark-green powder, on mixing acetate of baryta with purpurate of ammonia; its aqueous solution is purple. *Purpurate of lime* is greenish-brown, and yields a purple solution with hot water. *Purpurate of magnesia* is very soluble. Purpuric acid readily dissolves in heated acetic acid, but not in tartaric, citric, or oxalic acid. (PROUT.)

ERYTHRIC ACID.—Brugnatelli, under this name (from *ερυθραινεῖν*, to redden), described a substance which Dr. Prout regards as the crystallized compound of nitric and purpuric acid and ammonia, above mentioned. It has been more fully examined under the name of Alloxan, by Liebig and Wöhler.

Abstract of the researches of Liebig and Wöhler relating to Uric Acid, and its compounds. (*Ann. de Ch. et Ph.*, LXVIII. 225; *Chimie Organique*, p. 203.)—Liebig commences his account of these substances by assuming the existence of a basic radical, which he represents as a compound of 2 atoms of cyanogen and 4 of carbonic oxide, or by the ultimate formula ($2\text{car} + 2\text{n} + 4\text{o}$). To this base he applies the term *uril*, *urilic acid*, or *cyanoxalic acid*; and he observes that its elements are equivalent to those of oxalic acid, in which an atom of oxygen has been replaced by cyanogen: thus



Representing this base by the symbol *ul*, the formulæ of its compounds are as follow:—

Rational.	Empirical.
$2\text{ul} + 1\text{urea} = \text{Uric acid}$	$10\text{car} + 4\text{n} + 4\text{h} + 6\text{o}$
$2\text{ul} + 2\text{o} + 4\text{q} = \text{Alloxan}$	$8\text{car} + 2\text{n} + 4\text{h} + 10\text{o}$
$2\text{ul} + \text{o} + 5\text{q} = \text{Alloxantin}$	$8\text{car} + 2\text{n} + 5\text{h} + 10\text{o}$
$2\text{ul} + \text{A} + 2\text{q} = \text{Uramil}$	$8\text{car} + 3\text{n} + 5\text{h} + 6\text{o}$

ALLANTOIN. ALLANTOIC ACID. ($4\text{car} + 3\text{h} + 2\text{n} + 3\text{o}$) or ($2\text{cy} + 3\text{q}$).—This product, originally discovered by Vauquelin and Buniva in the allantoic fluid of the cow, has been artificially obtained by Liebig and Wöhler, by acting on uric acid by peroxide of lead. 1 part of uric acid is boiled in 2 (20?) of water, and peroxide of lead (pure and in fine powder) is added in successive portions as long as its colour changes; the hot liquor is then filtered and evaporated till crystals form upon its surface; when the solution is cold the crystals are purified by recrystal-

lization. They are small transparent prisms derived from the rhomboëdron, of a glassy lustre, tasteless, soluble in 160° of cold, and in less of boiling water; soluble in nitric acid, and decomposed by boiling, but without the evolution of nitrous fumes. Gently heated in sulphuric acid it is resolved into carbonic oxide, carbonic acid, and ammonia; if rapidly heated it is blackened. Boiled with caustic alkalis it yields an alkaline oxalate and ammonia, its composition being such that it contains the elements of oxalate of ammonia, minus 3 atoms of water. The caustic and carbonated alkalis may both dissolve it without decomposition, when aided only by a gentle heat. On adding a few drops of ammonia to a solution of allantoin in boiling water, a solution is obtained which gives a white precipitate with nitrate of silver, containing 43.54 per cent. of oxide of silver: its composition is represented by the formula $(3\text{ car} + 4\text{ n} + 5\text{ h} + 5\text{ o}) + (\text{ag} + \text{o})$, so that it contains 2 atoms of allantoin, minus 1 atom of water, which atom of water ($\text{h} + \text{o}$) is replaced by the atom of oxide of silver ($\text{ag} + \text{o}$).

When the mother liquor, which in this process for obtaining allantoin has deposited the crystals of that substance, is evaporated to the consistence of syrup, it deposits crystals of urea, and the white powder into which the oxide of lead is converted is oxalate of lead; the theory of the formation, therefore, of the allantoin, may be represented as follows:—

Atoms.	Car.	Hyd.	Nit.	Oxy.	Lead.	Atoms.	Car.	Hyd.	Nit.	Oxy.	Lead.
1 Uric acid . . .	10	4	4	6		yield	2 Oxalic acid . . .	4		6	
2 Peroxide of lead . . .				4	2		2 Protoxide of lead . . .				2
3 Water . . .		3		3			1 Allantoin . . .	4	3	2	3
							1 Urea . . .	2	4	2	2
	10	7	4	13	2			10	7	4	13
											2

ALLOXAN. $(3\text{ car} + 4\text{ h} + 2\text{ n} + 10\text{ o})$.—This term is applied by Wöhler and Liebig to the erythric acid of Brugnatelli. They obtained it by adding 1 part of uric acid in successive portions to 4 of nitric acid (specific gravity 1.45 to 1.5). It is dissolved with effervescence and evolution of heat, but the increase of temperature should be avoided by keeping the mixture cold, and adding the uric acid gradually. White and brilliant granular crystals are formed, and the liquid soon concretes; this mass should then be drained in a funnel and afterwards dried on a porous brick, and purified by solution in water and recrystallization.

Alloxan crystallizes from a solution which is not saturated, in colourless rhombic octoëdra, which are brilliant, and sometimes an inch in diameter; they are efflorescent, and lose 25 per cent. of water; they become anhydrous when gently warmed. A hot saturated solution deposits it at once in anhydrous prismatic crystals. It is very soluble in water, has a nauseous odour and slightly astringent taste. It reddens vegetable blues, and tinges the epidermis purple. By the action of alkalis it is converted into alloxanic acid. Boiled with an alkali it is transformed into urea and mesoxalic acid. Heated with peroxide of lead it forms urea and carbonate of lead, with traces of oxalate of lead. By sulphuretted hydrogen, or chloride of zinc, it is converted into alloxantin. Excess of ammonia transforms it into mycomelinic acid; nitric acid converts it into parabanic acid; and sulphuric acid or hydrochloric acid into alloxantine. By sulphurous acid and ammonia it is changed into thionurate of ammonia; and alloxantine and ammonia convert it into murex-

ide. By the joint action of a protosalt of iron and an alkali it forms an indigo-blue solution. It does not combine without decomposition with metallic oxides.

The formation of alloxan and other accessory products depends on two simultaneous distinct decompositions; namely, the conversion of uril (cyanoxalic acid) into alloxan, and the decomposition of urea by nitric acid. The nitric acid produces hyponitrite of ammonia and cyanic acid; the hyponitrite of ammonia is resolved by heat into nitrogen and water, while the cyanic acid with the elements of water yields carbonic acid, and ammonia.

	Carbon.	Hydrogen.	Nitrogen.	Oxygen.
Uril or cyanoxalic acid	8	.	2	4
4 atoms of water	.	4	.	4
2 „ oxygen	.	.	.	2
Alloxan	8	4	2	10

	Car.	Hyd.	Nit.	Oxy.		Car.	Hyd.	Nit.	Oxy.	
Urea	2	4	2	2	=	Carbonic acid	2	.	4	
						Nitrogen	2	.
Hyponitrous acid	.	.	1	3		Ammonia	3	1	.
						Water	1	.	1
	2	4	3	5		2	4	3	5	

ALLOXANIC ACID. ($3\text{car} + 2\text{n} + 2\text{h} + 3\text{o}$).—This acid has been mentioned as produced by the decomposition of alloxan by alkalis: it is obtained by decomposing alloxanate of baryta by sulphuric acid; a very acid solution is obtained, which yields groups of acicular crystals on evaporation, and dissolves zinc with the evolution of hydrogen: it is unchanged by sulphuretted hydrogen: in its free state it does not precipitate the salts of silver, baryta, or lime. The anhydrous alloxanic acid contains the elements of an atom of alloxan, minus 2 atoms of water.

Alloxanic acid neutralizes the alkalis, and decomposes the carbonates; the neutral alloxanate of ammonia gives a white precipitate with the salts of silver, which becomes yellow when boiled, and then black, and occasions an effervescence: supersaturated by ammonia it produces white gelatinous precipitates in the salts of lime, baryta, and strontia, which dissolve in excess of water, and very readily in the acids. The solution of the neutral alloxanates of lime, baryta, and strontia, become turbid by ebullition, and the precipitate which falls is a mixture of mesoxalate, carbonate, and alloxanate of the base, urea and mesoxalic acid remaining in the solution.

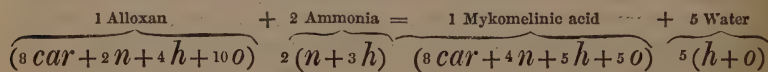
Alloxanate of Baryta. ($3\text{car} + 2\text{n} + 2\text{h} + 3\text{o}$) + ($\text{ba} + \text{o}$) + 3q .—Prepared by adding baryta water to an aqueous solution of alloxan, saturated when cold, and heated to 140° , so that the product disappears on stirring: as soon as the precipitate tends to permanence, a few drops of alloxan are added, to cause it to disappear, and the liquid on cooling yields alloxanate of baryta in small transparent needles, or in nacreous scales, which become opaque at 212° , and lose 6 atoms of water: at 300° they become anhydrous.

Alloxanate of Silver ($3\text{car} + 2\text{n} + 2\text{h} + 3\text{o}$) + ($\text{ag} + \text{o}$) is an anhydrous salt in the form of a white insoluble powder, which explodes slightly when heated.

MESOXALIC ACID. ($3car + 4o$).—When a saturated solution of alloxanate of baryta or strontia is heated to its boiling point, a precipitate falls, composed of the carbonate, mesoxalate, and alloxanate of baryta or strontia. On evaporating the solution crystalline crusts form, composed of urea and mesoxalate of baryta, which crusts, treated by alcohol, yield to it their urea, and the mesoxalate remains. If a solution of alloxane be dropped into a boiling solution of acetate of lead, a heavy granular precipitate of mesoxalate of lead is formed, and pure urea remains as the only product, in solution. The mesoxalic acid is obtained by the action of dilute sulphuric acid on the mesoxalate of baryta or of lead.

The solution of mesoxalic acid is very sour, reddens vegetable blues, crystallizes, and, like the alloxanic acid, produces, when saturated with ammonia, white precipitates in the salts of lime, baryta, and strontia, which are soluble in the acids and in excess of water. A solution of the mesoxalic acid may be boiled and evaporated without decomposition. The distinctive character of this acid is, that, when neutralized by ammonia and added to nitrate of silver, a yellow precipitate falls, which is reduced with effervescence to the metallic state, on being gently heated. The composition of the mesoxalate of lead is probably expressed by the formula $(3car + 4o) + 2(pl + o)$, in which case its formation from alloxan and alloxanic acid may be easily explained, for 1 atom alloxan $= (8car + 2n + 4h + 10o)$ minus 1 atom of urea $= (2car + 2n + 4h + 2o)$ leaves 2 atoms of mesoxalic acid $= 2(3car + 4o)$.

MYKOMELINIC ACID. ($8car + 4n + 5h + 5o$).—Prepared by boiling a solution of alloxan with excess of ammonia, then supersaturating with dilute sulphuric acid, and boiling for a few minutes; the mykomelinic acid forms a yellow gelatinous precipitate which dries into a porous powder, soluble in hot, but nearly insoluble in cold water; it is soluble in, and decomposed by boiling with, the fixed alkalis, when it evolves ammonia; it forms a yellow insoluble salt with oxide of silver. It is produced by the decomposition of 1 atom of alloxan and 2 of ammonia into 1 of mykomelinic acid and 5 of water.



PARABANIC ACID. ($6car + 2n + 4o$).—The crystallized acid contains 2 atoms of water. Prepared by mixing 1 part of uric acid or 1 of alloxan with 8 of nitric acid of mean strength, and evaporating to the consistence of syrup; colourless lamellar crystals gradually form, which are purified by recrystallization. Its taste is very acid; it is very soluble, and not efflorescent; when fused, part sublimes, and part is decomposed into hydrocyanic acid. On heating a solution of parabanic acid neutralized by ammonia, the acid is transformed into oxaluric acid.

OXALURIC ACID ($6car + 2n + 3h + 7o$) + ($h + o$) is prepared by adding dilute hydrochloric or sulphuric acid to a saturated and boiling solution of oxalurate of ammonia, and rapidly cooling the liquor; the oxaluric acid falls as a crystalline powder, which is washed with cold water till (as long as) the washings neutralized by ammonia produce with

the salts of lime a precipitate entirely soluble in hot water. It is a white crystalline powder, very acid, and when neutralized by ammonia forms with the salts of silver a white precipitate, soluble in boiling water. An aqueous solution of this acid is entirely resolved by boiling into oxalic acid and oxalate of urea. Oxaluric acid is formed by the union of 2 atoms of water with parabanic acid. The crystallized acid also includes the elements of 2 atoms of oxalic acid and 1 of urea; it may be considered as uric acid, in which the uril (or cyanoxalic acid) has been replaced by oxalic acid.

OXALURATES.—The oxaluric acid forms very soluble salts with the alkalis; with the alkaline earths its salts are almost insoluble. On mixing concentrated solutions of oxalurate of ammonia with chloride of calcium or of barium, transparent acicular crystals of oxalurate of lime or of baryta are formed. With excess of ammonia, oxalurate of lime yields a gelatinous precipitate soluble in great excess of water.

Oxalurate of Ammonia. $(6\text{ car} + 2\text{ n} + 3\text{ h} + 7\text{ o}) + (\text{n} + 4\text{ h} + \text{o})$.—This salt is formed directly by adding ammonia to a boiling solution of parabanic acid; or better by supersaturating with ammonia a recently-prepared solution of uric acid in nitric acid. The liquid, at first purple, becomes yellow by evaporation, and forms stellated groups of hard acicular crystals, which are purified by animal charcoal and recrystallization. The crystals are easily soluble in hot, but difficultly in cold water; the solution has no reaction on vegetable colours, and may be boiled and evaporated without change; the dry-salt loses no weight at 250° , but a higher temperature evolves hydrocyanic acid. The acids produce a crystalline precipitate of oxaluric acid in a concentrated solution of oxalurate of ammonia.

Oxalurate of Silver is obtained by mixing boiling solutions of oxalurate of ammonia and nitrate of silver; as the solution cools, anhydrous silky crystals are deposited, which at a high heat are decomposed without explosion; the formula of this salt is $(6\text{ car} + 2\text{ n} + 3\text{ h} + 7\text{ o}) + (\text{ag} + \text{o})$.

THIONURIC ACID. $(8\text{ car} + 3\text{ n} + 7\text{ h} + 14\text{ o} + 2\text{ s})$.—Prepared by decomposing thionurate of lead by sulphuretted hydrogen; it forms a mass of acicular crystals, unchanged in air, very soluble in water, and very acid; when its saturated solution is heated to the boiling point, it congeals into a semifluid crystalline mass of uramil, and the fluid contains free sulphuric acid. Thionuric acid contains the elements of 1 atom of alloxan, 1 of ammonia, and 2 of sulphurous acid; uramil may be regarded as a compound of ammonia with alloxan, *minus* 2 atoms of oxygen. On heating the solution of thionuric acid, 2 atoms of oxygen are given by 1 atom of alloxan to the 2 of sulphurous acid, which is thus converted into sulphuric acid, while the elements of uril, (or cyanoxalic acid,) ammonia, and water, combine to form uramil.

THIONURATES.—Thionuric acid forms very soluble salts with the alkalis; those with the alkaline earths are insoluble or sparingly soluble in water, but readily soluble in dilute acids; they generally contain 1 atom of acid and 2 of base: all these salts evolve sulphurous acid, when acted

on by sulphuric acid; fused with potassa they leave a residue of sulphite of potassa.

Thionurate of Ammonia is obtained by adding excess of sulphurous acid to a cold aqueous solution of alloxan, and then adding carbonate of ammonia as long as it effervesces, and afterwards excess of pure ammonia, and boiling for half an hour; as the solution cools, thionurate of ammonia crystallizes, and may be washed and dried. It forms quadrangular crystals of a pearly lustre, which become red at 212° , and lose 6 per cent. = 2 atoms of water; they are sparingly soluble in cold, and readily so in boiling water. When a solution of this salt is heated with a weak mineral acid, it suffers a decomposition similar to that of the thionuric acid. Mixed with nitrate of silver a brilliant film of the metal is gradually deposited. On evaporating thionurate of ammonia on a water-bath, with the addition of a quantity of sulphuric acid less than sufficient to neutralize its ammonia, white acicular crystals of acid thionurate of ammonia are obtained, which by boiling are resolved into uramilic acid and ammonia.

Thionurate of Lead is obtained by double decomposition in the form of a gelatinous precipitate, which quickly changes in a hot solution into short white needles; on drying they lose water, and become pink; exposed to destructive distillation, urea, and a substance which forms large broad crystals, are the results.

URAMIL. ($^3 \text{car} + ^3 \text{n} + ^5 \text{h} + ^6 \text{o}$).—A product of the decomposition of thionuric acid, obtained by heating a cold saturated solution of thionurate of ammonia to its boiling point, then adding excess of hydrochloric acid, heating again till it becomes slightly turbid, and allowing it to cool slowly; or a boiling saturated solution of the same salt may be mixed with hydrochloric or dilute sulphuric acid, and boiled till the whole forms a semifluid mass; it yields plumose acicular crystals permanent in the air, but becoming pink when heated; insoluble in cold, but slightly soluble in boiling water; soluble in ammonia and the caustic alkalis in the cold, and precipitated from them unchanged by acids. The solution of uramil in ammonia and in caustic potassa becomes purple by exposure to air, and deposits green acicular crystals of a metallic lustre; if boiled with caustic potassa, ammonia is evolved, and uramilic acid formed. Uramil is soluble in sulphuric acid, from which it is thrown down by water; boiled in dilute acids, it suffers the same changes as with potassa; by boiling with oxide of silver and of mercury, it is converted into murexid, and the metal is reduced. Nitric acid converts it into alloxan, hyponitrous acid being evolved and nitrate of ammonia formed. Uramil is formed in the above process by the separation of 2 atoms of sulphate of ammonia. Uramil may be considered as uric acid in which the urea is replaced by 1 atom of ammonia and 2 of water.

URAMILIC ACID ($^{16} \text{car} + ^5 \text{n} + ^{10} \text{h} + ^{15} \text{o}$) is a product of the decomposition of uramil; it is obtained by adding a cold saturated solution of thionurate of ammonia to a small quantity of sulphuric acid, and evaporating the mixture in a water bath, when uramilic acid is slowly deposited in transparent prisms. If a white deposit soluble in hot water is at the same time formed, it arises from undecomposed acid thionurate

of ammonia, which must be redissolved, and treated by sulphuric acid as before.

Uramilic acid forms acicular four-sided prisms, soluble in 6 to 8 of cold, and 3 of boiling water; does not lose weight, but becomes pink at 212° ; soluble in sulphuric acid with effervescence, but does not colour the acid. Boiled with nitric acid, it yields a yellow solution, and on evaporation, white scaly or granular crystals, soluble in the alkalis, and again precipitated by acetic acid. In the formation of uramilic acid 2 atoms of uramil lose the elements of 1 of ammonia, which are replaced by 3 of water.

Uramilic acid forms soluble crystallizable salts with ammonia, and with the fixed alkalis; the salts of lime and baryta are not precipitated by the free acid, but a white precipitate is formed on the addition of ammonia, which is redissolved by excess of water. Uramilate of ammonia produces a dense white precipitate with nitrate of silver containing about 63 per cent. of silver.

ALLOXANTIN. ($8\text{ car} + 2\text{ n} + 5\text{ h} + 10\text{ o.}$).—The formation of this substance was first remarked by Prout in the decomposition of uric acid by nitric acid. Wöhler and Liebig obtained it by the action of chlorine on uric acid, or by that of deoxidizing agents upon alloxan. *From uric acid*: 1 part of uric acid is added to 32 of water, heated to its boiling point, and then treated with dilute nitric acid in successive portions till dissolved; it should then be evaporated to two-thirds its volume, and after standing for some time crystals of alloxantin are deposited, which should be purified by recrystallization. *From alloxan*: by passing sulphuretted hydrogen into a solution of alloxan; sulphur is first deposited, and then a crystalline mass of alloxantin; it is separated from the sulphur by hot water, and the solution yields it in crystals on cooling. When a solution of alloxan is subjected to voltaic electricity, oxygen is evolved at the positive electrode, and the negative becomes covered with a crystalline crust of alloxantin. Alloxantin forms short oblique four-sided prisms, colourless, or slightly yellow; in an ammoniacal atmosphere they redden, and then acquire a greenish hue, and become pulverulent; they lose no weight till heated to 300° , when they lose 15.4 per cent. of water = 3 atoms. They are little soluble in cold, but more so in boiling water; the solution reddens litmus. Heated with solution of chlorine alloxantin becomes alloxan; with solutions of silver, it produces a black metallic precipitate. Alkalis decompose alloxantin; with baryta water it gives a violet precipitate, which first becomes colourless and then disappears when heated.

The *formation* of alloxantin is as follows: by the action of nitric acid the uril (cyanoxalic acid) of the uric acid combines with 1 atom of oxygen, and with the elements of 5 atoms of water, to form 1 atom of alloxantin, and nitrous acid, which latter is decomposed by the water into hyponitrous and nitric acid. In its preparation by alloxan, 1 atom of the latter is converted by the hydrogen of the sulphuretted hydrogen into water, which remains in combination with the other elements. On boiling alloxan with sulphuric acid, 2 atoms are resolved into 1 of alloxantin, 3 of oxalic acid, 1 of ammonia, and 1 of cyanic acid, the latter being

decomposed, together with 3 atoms of water, into carbonic acid and ammonia.

When sulphuretted hydrogen is passed through a boiling solution of alloxantin, sulphur is thrown down, and the solution becomes strongly acid; if neutralized by carbonate of ammonia, it deposits silky white crystals on cooling, of an ammoniacal salt, which becomes red when heated to 212° , and which appears to be a compound of cyanoxalic acid with 1 atom of ammonia, and 4 of water; it is represented by the formula ($3\text{ car} + 3\text{ n} + 7\text{ h} + 3\text{ o}$). The acid of this salt appears at the moment of its separation from the ammonia to be resolved into several new products; it is proposed to call it *dialuric acid*, since its properties differ essentially from those of the urilic (or cyanoxalic) acid. One of the products of its decomposition is obtained by dissolving it in dilute sulphuric or hydrochloric acid, and exposure to air; it forms hard colourless crystals corresponding in chemical properties with alloxantin, but differing from it in their form; it may be called *dimorphous alloxantin*. The same substance is obtained when uramil or uramilic acid is heated with dilute hydrochloric or sulphuric acid till entirely decomposed.

When a hot saturated solution of alloxantin is mixed with a solution of sal ammoniac, it immediately becomes purple, but this colour soon disappears, and the solution deposits white scales of uramil which become pink when dried; the same thing occurs with other salts of ammonia; the solution, after the above decomposition, contains free hydrochloric acid and alloxan. When a solution of alloxantin in ammonia which has been prepared cold is spontaneously evaporated, it absorbs oxygen, and crystals of oxalurate of ammonia are formed. 3 atoms of alloxantin, 7 of oxygen, and 6 of ammonia, contain the elements of 4 atoms of oxalurate of ammonia and 5 of water. When oxide of silver is heated in a solution of alloxantin, a portion of it is reduced with effervescence, and the solution contains pure oxalurate of silver. In this case, 3 atoms of oxygen from the oxide of silver decompose 1 of alloxantin into 1 of water, 2 of carbonic acid, and 1 of oxaluric acid, which last unites with undecomposed oxide of silver. Alloxantin dissolves peroxide of mercury without evolution of gas; the solution appears to contain alloxanate of protoxide of mercury. When a mixture of peroxide of lead and alloxantin are boiled together, urea and carbonate of lead are produced.

MUREXID.—This term has been applied by Liebig and Wöhler to Dr. Prout's *purpurate of ammonia*: its ultimate composition is very uncertain; the most consistent formula is apparently ($12\text{ car} + 5\text{ n} + 6\text{ h} + 3\text{ o}$). The following is Liebig's account of its preparation and properties:—

“*Preparation*.—By heating a mixture of equal parts of peroxide of mercury and uramilic acid in 36 to 40 parts of water, with the addition of an exceedingly small quantity of ammonia; as soon as the liquid has acquired a deep purple colour, it is filtered and allowed to rest, when the murexid crystallizes; or by dissolving uramil by the aid of heat in ammonia, and when the solution has cooled to 160° , alloxan is added until a very slight alkaline reaction is observed. Or a solution of uric acid in dilute nitric acid is evaporated until it acquires a flesh-red colour, when it is allowed to cool to 160° , and is then treated with a dilute

aqueous solution of ammonia, till the presence of free ammonia is remarked by the odour; the solution is then diluted with half its volume of boiling water, and allowed to cool. In applying this method of preparation it is advisable to test a small quantity of the solution of uric acid from time to time by saturating it with ammonia: if it be rendered turbid by the ammonia, and a red powder falls, a small quantity of nitric acid must be added to the hot solution of the uric acid; but if a yellow slimy precipitate be formed, the solution will only give rise to the formation of murexid after a stream of sulphuretted hydrogen has been transmitted through it. Or a boiling saturated solution of alloxantin in water is treated with ammonia in excess till the precipitated uramil is redissolved, when a solution of alloxan is added, so that only a slight alkaline reaction is left, and the whole is allowed to cool. Or by heating alloxantin with sal-ammoniac or oxalate of ammonia, and after the formation of uramil adding ammonia till the former is redissolved, and then alloxan. Murexid may be formed by a number of other processes, by bringing together many of the products of uric acid with ammonia, with or without the presence of atmospheric air.

“When the oxygen from $1\frac{1}{2}$ eq. of peroxide of mercury is added to 2 eq. uramil, they may give rise to the formation of 1 eq. murexid, 1 eq. alloxanic acid, and 3 eq. water. Alloxan appears to have the same action upon a solution of uramil in ammonia as the peroxide of mercury. One eq. alloxan, 2 eq. alloxantin, and 4 eq. ammonia, contain the elements of 2 eq. murexid and 14 eq. water. The solution of uric acid in dilute nitric acid contains principally alloxantin, urea, and nitrate of ammonia: evaporated until the flesh-red colour appears, a portion of the alloxantin is converted by the action of free nitric acid into alloxan, a portion of which, by a further action, gives rise to parabanic acid. But when alloxan and alloxantin are simultaneously present in a solution, an excess of ammonia produces a deep purple-red liquid from which murexid is deposited. If the solution contain an excess of alloxantin, the crystals of murexid are mixed with uramil: with an excess of alloxan, mykome-linate of ammonia is formed, which also falls with the murexid. The parabanic acid present passes, when the solution of uric acid is saturated with ammonia, into oxaluric, which is obtained in crystals of oxalurate of ammonia by evaporating the mother-liquor.

“*Properties.*—Murexid crystallizes in short four-sided prisms, two faces of which, like the upper wings of the cantharides, reflect a green metallic lustre. The crystals are transparent, and by transmitted light are of a garnet-red colour. It forms a brownish-red powder, which, under the polishing steel, acquires a brilliant metallic green colour. It is insoluble in ether and alcohol; sparingly soluble in cold, but more readily in boiling water, on the cooling of which it crystallizes unchanged; insoluble in a saturated solution of carbonate of ammonia; soluble in caustic potassa with a beautiful indigo-blue colour, which disappears on the application of heat with the evolution of ammonia. It is decomposed either in the solid state or in solution by all the mineral acids, with the separation of brilliant scales of murexan: the liquid contains ammonia, alloxantin, alloxan, and urca. The instant the murexid is brought into contact with hydrosulphuric acid it is decomposed into alloxantin, dia-

luric acid, and murexan, with the separation of sulphur. An equivalent of alloxan, alloxantin, murexan, and urea, together with 2 eq. ammonia, contain the elements of 2 eq. murexid and 11 eq. water."

MUREXAN.—"The purpuric acid discovered by Prout as the product of the decomposition of murexid. Its formula is ($6\text{ car} + 2\text{ n} + 4\text{ h} + 5\text{ o}$). Prepared by dissolving murexid in caustic potassa by the aid of heat, which is applied till the blue colour disappears, when dilute sulphuric acid is added in excess.

"Properties.—It falls in crystalline scales of a silky lustre; is insoluble in water and dilute acids, but is taken up by ammonia and the fixed alkalis in the cold without neutralizing them. It is dissolved by concentrated sulphuric acid, from which it is again precipitated unchanged by water. If a solution of murexan in ammonia be exposed to the air, it acquires a purple-red colour, and deposits the brilliant crystals of murexid; with an excess of ammonia the solution again becomes colourless, and is then found to contain oxalurate of ammonia. 2 eq. murexan, 1 eq. ammonia, and 3 eq. oxygen, contain the elements of 1 eq. murexid and 3 eq. water; 1 eq. murexan, 3 eq. oxygen, and 1 eq. ammonia are the constituents of 1 eq. oxalurate of ammonia*." (Liebig and Wilton Turner's edition of the late Dr. TURNER'S *Elements of Chemistry*, p. 820.)

COMPOSITION OF URINE IN DISEASES.—The urine is liable to infinite modifications both in the quantity and quality of its components, and when these are regular or constant, or when they exceed certain limits, they are regarded as constituting morbid states of the secretion.

I have already adverted to the new characters which the urine sometimes acquires from particular kinds of food or medicine. Odorous principles are often carried off by it, as in the case of asparagus, oil of turpentine, and several other varieties of volatile oil. During a course of

* The preceding details are taken from the French edition of Liebig's work on organic chemistry, and from the *Elements of Chemistry*, by Turner and Liebig. Dr. Prout observes that, "before he can subscribe to the accuracy of Liebig and Wöhler's analyses, they must be better authenticated than they are at present: I know at present of no apparatus or means of operating capable, when azote is concerned, of unequivocally deciding about the presence or absence of *one proportion* of hydrogen or even of oxygen in a complicated body. Liebig's analytical apparatus was in effect tried by me nearly 20 years ago, and for *rude approximations* it answers very well, but it is not in my opinion at all adapted for obtaining *very accurate* results. There is another circumstance which makes me hesitate to receive these results with confidence. I long ago settled, to my

own satisfaction, that the combining weight of carbon is neither more nor less than *six*, whereas, most foreign chemists, following Berzelius, make the combining weight considerably higher. Since the above was in type, I observe that Dumas has proved by a very elaborate series of experiments, that the combining weight of carbon is really *six*, hydrogen being unity." Dr. Prout also protests against the barbarism of Liebig and Wöhler's new terms, "particularly," he adds, "as I am by no means satisfied that the doctrines on which they are founded are satisfactorily established." I quote these remarks from so high and cautious an authority under a conviction of their justice and importance; our young chemists are especially addicted to the equivalents and formulæ and symbols of the foreign schools, apparently merely because they are foreign.

mercurial friction, mercury is said to have been found in the sediment, which, in such cases, is generally deposited; and traces of iron have been found during a course of chalybeate remedies. Nitre, ferrocyanuret, and sulpho-cyanuret of potassium, iodine, and iodic salts, several borates, carbonates, chlorates, and even silicates, and many of the acids and alkalis, have also been traced passing off from the stomach by the kidneys; some of the vegetable salts with alkaline bases appear to suffer such decomposition, as to act upon the urine in the manner of free alkalis, the acid being decomposed, probably by the process of digestion. Among the substances which pass off by urine, none are more remarkable, or more easily observed, than colouring-matters of vegetable origin, such as those of many fruits, logwood, madder, rhubarb, and also several astringents; these sometimes are not apparent, till the urine is tested by an alkali, or by solution of iron. The mineral acids, alcohol, ether, camphor, empyreumatic oils, musk, the colouring-matters of cochineal, litmus, and *sap-green* (which is the green extractive of the *Rhamnus catharticus*) and others, insoluble in water, are said not to pass by urine in an unchanged state.

In many diseases, there is an excessive secretion of *acid* along with the urine; this is sometimes *uric acid*, which we shall presently refer to, and sometimes oxalic or even nitric acid, neither of which belong to healthy urine; I have also observed a peculiar acid state of urine depending upon a volatile acid, which I believe to be either the acetic or lactic. Nor is an alkaline state of urine, or at least a deficiency in the proper proportion of acid, at all uncommon; it is often the result of particular food and medicine, and sometimes habitual; in such cases, the urine has a tendency to a white deposit, or film; and is generally opalescent, when voided, or speedily becomes so. This is generally the case in injuries of the spine affecting the nerves which supply the kidneys, and in these cases ammoniacal urine is sometimes voided.

The relative proportion of urea fluctuates on one side or other of the healthy standard, from a variety of causes: when it is defective, the urine loses its putrefactive tendency, and when long boiled or heated, there is not that production of ammonia which belongs to healthy urine. In inflammatory affections of the liver, in hysteria, in some cases of excessive secretion of albuminous matter, and in some of diabetes, there is this deficiency of urea. In other cases, urea is in excess, so that nitric acid added to the urine causes a deposition of nitrate of urea. Dr. Prout judges of the presence of excess of urea, by putting the urine into a watch-glass, and dropping in a little nitric acid, so as to collect at the bottom; if there be a separation of crystals of nitrate of urea in the course of less than half an hour, that ingredient is probably present in morbid proportion.

Albumen is a common ingredient in healthy urine, but always in very small relative proportion; in some cases of disease, it is so abundant as to coagulate by heat, or even sometimes, spontaneously, within the bladder: it is also recognised by the precipitate which it affords to ferrocyanuret of potassium; but in applying this test, and, indeed, generally, in judging of the state of the urine of any individual, it should be previously ascertained that it is not naturally subject, (which is at times the case,) to excess or deficiency of this, or others of its components. In some forms

of dropsy, especially where there is renal disease, excess of albumen is often observed; in these instances the urine is scanty, and its specific gravity below the usual average, in consequence of deficiency in saline matter and in urea; and it deserves notice, that in some such cases urea has apparently existed in the blood.

A peculiar *red* colouring-matter, differing from any uric or purpuric combination, is sometimes present in the urine, associated with the late-ritious sediment; it is soluble in alcohol, but has not been accurately examined. Messrs. Brett and Bird have adverted to such cases in a paper published in the *Medical Gazette*, for August, 1834. A *blue* and *black* colouring matter have been observed in the urine, but they are of very rare occurrence; the former is the *cyanurin* of Braconnot, and the latter the *melanic acid* of Prout? These appear to be peculiar organic compounds; the former has apparently been mistaken for Prussian blue. The yellow, brown, or green tint, which urine sometimes acquires, in jaundice and obstructions of the liver, seems to depend upon the presence of bile or of its colouring matter. In these cases, hydrochloric acid brightens the colour, or renders it green.

The most extraordinary morbid change which urine suffers, is that connected with the formation of sugar in the disease called *diabetes*. This urine does not easily putrefy, and may be made to undergo vinous fermentation; it is usually of a pale colour, and more or less sweet to the taste, and its specific gravity commonly above the healthy standard*; it is not, as is often supposed, destitute of, and even generally, I believe, not deficient in, urea.

* The following table, constructed by Dr. Henry, shows the quantity of solid extract, in a wine-pint of urine of different specific gravities, from 1·020, to 1·050. In the experiments which furnished the data of this table, the urine was evaporated by a steam-heat till it ceased to lose weight, and left an extract which became solid on cooling. (*Med. Chir. Trans.*, ii. 118.) This is a useful table to the medical practitioner, who, in cases of diabetes, may draw important inferences respecting the progress of the disease, and the influence of medicines, from the differing density of the urine.

Specific gravity compared with 1000 parts of water at 60°.	Quantity of solid extract in a wine-pint.	Quantity of solid extract in a wine-pint, in	Specific gravity compared with 1000 parts of water at 60°.	Quantity of solid extract in a wine-pint.	Quantity of solid extract in a wine-pint, in
	grs.	oz. dr. scr. grs.		grs.	oz. dr. scr. grs.
1020	382·4	0 6 1 2	1036	689·6	1 3 1 9
1021	401·6	0 6 2 1	1037	708·8	1 3 2 8
1022	420·8	0 7 0 0	1038	728·0	1 4 0 8
1023	440·0	0 7 1 0	1039	747·2	1 4 1 7
1024	459·2	0 7 1 19	1040	766·4	1 4 2 6
1025	478·4	0 7 2 18	1041	785·6	1 5 0 5
1026	497·6	1 0 0 17	1042	804·8	1 5 1 4
1027	516·8	1 0 1 16	1043	824·0	1 5 2 3
1028	536·0	1 0 2 16	1044	843·2	1 6 0 3
1029	555·2	1 1 0 15	1045	862·4	1 6 1 2
1030	574·4	1 1 1 14	1046	881·6	1 6 2 1
1031	593·6	1 1 2 13	1047	900·8	1 7 0 0
1032	612·8	1 2 0 12	1048	920·0	1 7 1 0
1033	632·0	1 2 1 12	1049	939·2	1 7 1 19
1034	651·2	1 2 2 11	1050	958·4	1 7 2 18
1035	670·4	1 3 0 10			

Diabetic Sugar may be obtained by evaporating such urine to the consistency of syrup, and keeping it in a warm place, when a granular mass is obtained which must be washed with cold alcohol to abstract the colouring matter; it may then be dissolved in boiling alcohol, and purified by repeated solution and crystallization, or by the help of animal charcoal. It is a granular sugar, resembling grape sugar in appearance and composition: it consists, according to Prout, of 40·00 carbon, 6·67 hydrogen, and 53·33 oxygen, per cent.

The following analyses of diabetic urine are by Meisner; the different samples were taken at different periods from the same individual.

	I.	II.	III.
Substances soluble in ether: urea, lactic acid, lactate of lime, extractive	0·34 . .	0·33 . .	0·65
Substances soluble in alcohol: sugar, extractive, salts	7·06 . .	3·46 . .	5·78
Substances soluble in water: extractive, salts	1·37 . .	3·44 . .	0·99
Mucus, with phosphate of lime and traces of oxide of iron	0·34 . .	0·31 . .	0·46
Water	91·19 . .	92·46 . .	92·10

In *diabetes insipidus*, the urine, though not sweet, is excessive in quantity, and deranged as to composition. The formation of urea is suspended, and such urine leaves, on evaporation, a brown residue, of the consistence of syrup, from which nothing crystallizes, and which is slightly acid. Alcohol of ·830 dissolves the greater part of this residue, and leaves, on evaporation, a yellow, deliquescent extractive matter, which resembles that which similar alcohol extracts from the inspissated decoctions of muscular flesh. The portion insoluble in alcohol, appears also to partake of the same properties. (BERZELIUS.)

CALCULOUS CONCRETIONS.—It frequently happens that certain ingredients in the urine are secreted in excess, or that, from other causes, they are deposited in a solid form, constituting *sand*, *gravel*, and *calculi*.

Sabulous depositions in the urine are of various characters, but, as far as their leading chemical varieties are concerned, they may be conveniently termed *white sand* and *red sand*; the former consisting usually of *phosphate of lime*, or *ammonio-magnesian phosphate*, or of mixtures of the two; whilst, in the latter, *uric acid* predominates. These deposits are frequently temporary only, and may be produced by a variety of accidental causes, which influence the secretion of urine; but when they are more or less constant, or arise from very trifling causes, they then require the utmost attention, as being frequent forerunners of calculus. This tendency to the deposition of solid matter is generally first observed in the urine after it is voided, and as it cools; but it afterwards increases to such an extent that it is voided more or less turbid; and, at length, symptoms of gravel or of stone in the kidney or bladder ensue.

Urinary calculi are composed either of materials that exist at all times in the urine, or of substances which only occasionally appear, and which may, therefore, be regarded as products of disease. The following are their component ingredients:—

- | | |
|---------------------------------|-----------------------|
| 1. Uric or lithic acid. | 6. Cystic oxide. |
| 2. Urate of ammonia. | 7. Carbonate of lime. |
| 3. Phosphate of lime. | 8. Xanthic oxide. |
| 4. Ammonio-magnesian phosphate. | 9. Silica. |
| 5. Oxalate of lime. | |

Of these substances, the first five are of most frequent occurrence, but their relative frequency varies in different countries and districts. Dr. Yelloly, in a paper on the "Tendency to Calculous Diseases," (*Phil. Trans.*, 1829,) has given the following view of the different descriptions of calculi contained in the collection belonging to the Norwich hospital: from this table it will be seen that about one-half of the specimens are composed of one description of material only; and that the remainder consist of alternating layers, more or less numerous, of most of the substances of which human urinary calculi are composed.

Calculi consisting principally of one deposit.

Lithic acid	81
Lithate of ammonia	20
Oxalate of lime	20
Phosphate of lime	4
Fusible calculus, or mixed phosphates; that is to say, calculi composed of the triple, or ammoniaco-magnesian phosphate, mixed with phosphate of lime	37

Calculi consisting of two deposits.

Lithic acid and lithate of ammonia	37
" oxalate of lime	11
" mixed phosphates	10
" phosphate of lime	2
Lithate of ammonia and lithic acid	2
" oxalate of lime	25
" mixed phosphates	14
" phosphate of lime	1
Oxalate of lime and lithic acid	10
" lithate of ammonia	1
" mixed phosphates	15
" phosphate of lime	3
Mixed phosphates and phosphate of lime	2

Calculi consisting of three deposits.

Lithic acid, phosphate of lime, and mixed phosphates	2
" oxalate of lime, and phosphate of lime	1
" oxalate of lime, and lithate of ammonia	2
" oxalate of lime, and lithic acid	4
" lithate of ammonia, and oxalate of lime	2
" oxalate of lime, and mixed phosphates	1
Lithate of ammonia, oxalate of lime, and mixed phosphates	3
" oxalate of lime, and lithic acid	8
" phosphate of lime, and lithate of ammonia	1
" lithic acid, and mixed phosphates	2
Oxalate of lime, lithic acid, and lithate of ammonia	1
" lithic acid, and oxalate of lime	1
" lithic acid, and mixed phosphates	2

Calculi consisting of four or more deposits.

Lithate of ammonia, oxalate of lime, lithic acid, and mixed phosphates	1
Oxalate of lime, lithic acid, oxalate of lime, and mixed phosphates	1
Lithate of ammonia, oxalate of lime, phosphate of lime, oxalate of lime, and lithate of ammonia	1

In the last edition of Dr. Prout's work *On the Nature and Treatment of Stomach and Urinary Diseases*, there is a valuable table in which the urinary calculi contained in the museums of Bartholomew's and Guy's hospitals, and in the provincial hospitals of Norwich, Manchester, and Bristol, are contrasted with the calculi existing in Swabia and Copenhagen; this table is interesting, as showing the relative prevalence of the different species of calculi, and the order of succession of their different layers.

1. *Calculi composed of uric acid*, of which acid the chemical properties have already been described, are of a brown or fawn colour; and, when cut through, appear of a more or less distinctly laminated texture. Their surface is generally smooth, or nearly so, being sometimes slightly tuberculated. Before the blowpipe, this calculus blackens, and gives out a peculiar ammoniacal odour, leaving a minute portion of white ash: it is soluble in solution of pure potassa, and, heated with a little nitric acid, affords the red compound above-mentioned.

2. *Urate of ammonia* forms calculi, the surface of which is sometimes smooth, sometimes tuberculated: they are made up of concentric layers, and the fracture is fine earthy, resembling that of compact limestone; they are generally of a small size, and rather uncommon, though urate of ammonia often occurs mixed with uric acid. It usually decrepitates before the blowpipe, is more soluble than the uric calculus, evolves ammonia when heated with solution of potassa, and is readily soluble in the alkaline carbonates, which pure uric acid is not.

3. *Phosphate of lime calculus* is of a pale-brown or gray-colour, smooth, and made up of regular and easily-separable laminæ. It is soluble in hydrochloric acid, and precipitated by pure ammonia, and does not fuse before the blowpipe. *Calculi from the prostrate gland* are frequently composed of phosphate of lime.

4. *Ammonio-magnesian, or triple calculus*, is generally white, or pale-gray, and the surface often presents minute crystals; its texture is generally compact, and often somewhat hard and translucent; heated by the blowpipe, it exhales ammonia, and leaves phosphate of magnesia. It is more easily soluble than the preceding; and oxalate of ammonia forms no precipitate in its hydrochloric solution.

It frequently happens that calculi consist of a mixture of the two last-mentioned substances, in which case they fuse before the blowpipe, and are hence termed *fusible calculi*. They are white, or nearly so, and softer than the separate substances, often resembling chalk in appearance. They are easily soluble in hydrochloric acid, and if oxalate of ammonia be added to their solution, the lime is precipitated in the state of oxalate.

5. *Oxalate of lime* forms calculi, the exterior colour of which is generally dark-brown, or reddish; they are commonly rough or tuberculated upon the surface, and have hence been called *mulberry calculi*. Before the blowpipe, they blacken and swell, leaving a white infusible residue, which is easily recognised as quicklime. Small oxalate of lime calculi are, however, sometimes perfectly smooth upon the surface, and somewhat resemble a hempseed in appearance.

6. *Cystic oxide* is a peculiar animal substance; the calculi composed of it, which are rare, are in appearance most like those of the ammonio-

magnesian phosphate. They are soft, and when burned by the blowpipe, exhale a peculiar foetid odour. They are soluble in nitric, sulphuric, hydrochloric, phosphoric, and oxalic acids, and also in alkaline solutions. Cystic oxide forms crystallizable compounds with nitric, hydrochloric, and oxalic acids. With sulphuric acid it forms a viscid, colourless, and uncrystallizable compound. Its component parts, according to Prout, are carbon 29.9, hydrogen 5.1, oxygen 53.1, nitrogen 29.9. A specimen from a dog, analyzed by Lassaigne (*Ann. de Ch. et Ph.*, xxiii. 329), yielded carbon 36.2, nitrogen 34.0, oxygen 17.0, hydrogen 12.8; but it is probable that these were different substances. The cystic oxide, according to the analysis of Thaulow, is represented by the formula ($6\text{ car} + n + 6\text{ h} + 4\text{ o} + 2\text{ s}$). It contains:—

				Thaulow.
Carbon . . .	6 . . .	36 . . .		30.31
Nitrogen . .	1 . . .	14 . . .		11.71
Hydrogen . .	6 . . .	6 . . .		4.94
Oxygen . . .	4 . . .	32 . . .		26.47
Sulphur . . .	2 . . .	32 . . .		26.58
Cystic oxide	1	120		100.00

7. Dr. Prout, and Mr. Smith of Bristol, (*Medico-Chir. Trans.*, xi. 14,) have described calculi composed almost entirely of *carbonate of lime*; but this species is exceedingly rare, and among several hundred calculi which I have examined, I never met with it from the human bladder. Carbonate of lime calculi are small, white, and friable. I have seen many beautiful specimens of carbonate of lime calculus from other animals. I have also observed very small and perfectly spherical concretions, composed of carbonate of lime and animal matter, voided in a case in which they apparently came from the prostrate gland. In the case of this calculus cited by Mr. Smith, several small ones were voided, and three large calculi of similar composition were removed by operation.

8. *Xanthic Oxide*. This substance has already been adverted to as discovered in a calculus by Dr. Marcet; Dr. Prout observes that he has never met with another specimen. "Some late writers," he observes, "assert that xanthic oxide forms a constituent of certain lithic acid calculi of a light or bright brown colour, and which exhibit a scaly shining fracture of a brown or deep flesh-colour, and yield a resinous lustre by friction. I cannot confirm or deny this statement. To obtain xanthic oxide Liebig directs us to dissolve the calculi containing it in caustic potassa, and saturate the solution with carbonic acid, which, he says, throws down xanthic oxide in the form of a white precipitate, which becomes hard and yellow by drying, and acquires a waxy lustre by friction. It is soluble in the pure and carbonated alkalis, but sparingly soluble in hot water and in hydrochloric and oxalic acids. It forms a deep yellow solution with concentrated sulphuric acid, which is not precipitated by water. Nitric acid dissolves it without effervescence, and on evaporation there remains a residue which is not reddened by ammonia, but is of a *lemon-yellow* colour and little soluble in water; the alkalis dissolve this residue, becoming deep yellow, and leave a residuum of a red colour on evaporation. Liebig represents xanthic oxide by the formula ($5\text{ car} + 2\text{ n} + 2\text{ h} + 2\text{ o}$).

9. *Silica*, as an ingredient in urinary sand and in some calculi, is very rare. It would appear from the statement of Mr. Venables (*Quart. Jour.*, N.S., December, 1829), that it most commonly is voided in the form of sand. Several supposed cases of siliceous sand have been traced to imposture. I have, however, seen, in the possession of Dr. Yelloly, an unequivocal specimen of siliciferous calculus; it was taken from a boy by an operation, and consisted chiefly of oxalate of lime, having small cavities in its interior, lined with an apparently chalcedonic crust, which, on examination, proved to be silica.

These are the principal chemical facts belonging to the history of urinary calculi. In Dr. Wollaston's valuable papers upon this subject (*Phil. Trans.*, 1797 and 1810), much additional information will be found. In the same work (1806, 1808, and 1810), I have given some account of their peculiarities, depending upon their situation, and have also discussed the chemical operation of *solvents*, a subject taken up more in detail in the *Quarterly Journal of Science and the Arts*, vol. viii. The late Dr. Marcet published a valuable dissertation on *Calculous Disorders*; but Dr. Prout's "Inquiry into the Nature and Treatment of Gravel, Calculus," &c., may be considered as the best medico-chemical work upon the subject.

URINE OF OTHER ANIMALS.—From comparative analyses of the urine of different animals, it appears that urea is present in the higher orders. The urine of carnivorous animals is at first acid, but becomes speedily alkaline, and is very prone to putrefaction; it generally contains uric acid, but in small quantity; the urine of graminivorous animals contains *hippuric* or *urobenzoic acid*, the formula of which is ($^{12}car + 8h + 5o + n$) + q : this acid becomes benzoic acid when the urine is evaporated at 212° . According to Hieronymi, as quoted by Berzelius, the urine of the *lion*, *tiger*, and *leopard*, is transparent, and of a nauseous odour and bitter taste; its specific gravity varies in the same individual, from 1.059 to 1.076. As soon as voided, it becomes alkaline from the formation of carbonate of ammonia. During evaporation it deposits white flakes, and when concentrated, part of the urea crystallizes. The urine of these animals yielded

Urea, extractive, and free acetic (lactic?) acid	13.220
Uric acid	0.022
Mucus	0.510
Sulphate of potassa	0.122
Hydrochlorate of ammonia, and chloride of sodium	0.116
Phosphate of lime and magnesia, with a trace of carbonate of lime	0.176
Phosphate of potassa and of soda	
Phosphate of ammonia	0.102
Acetate (lactate) of potassa	0.330
Water	84.600
	100.000

The urine of the *hyaena* and *panther* contained the same ingredients, the specific gravity of the former being 1.061, and of the latter, 1.045.

The urine of the *rhinoceros* is muddy, yellow, and, when exposed to air, acquires a crystalline film of carbonate of lime; it effervesces and

becomes clear on the addition of an acid. Left to itself, it deposits a yellow powder, composed of carbonate of lime and magnesia, traces of oxide of iron, of silica, and of an azotized animal matter; the clear portion, when evaporated, yields a similar precipitate, and on the addition of hydrochloric acid, deposits *urobenzoic acid*. (VOGEL.)

Elephants' urine is turbid from carbonate of lime and magnesia, it contains no *benzoate*, but much *urea*. (VOGEL.)

The urine of the *horse*, contains *urea* 0·7, *hippurate* of soda 2·4, carbonate of soda 0·9, chloride of potassium 0·9, carbonate of lime 0·2 to 1·1. Water 94·0. Chevreul found sulphate of lime.

The urine of the *camel* yielded carbonate of ammonia and volatile oil by distillation; sulphuric, nitric, and hydrochloric acid, reddened it: on evaporation it deposited carbonate of lime and of magnesia, with animal matter and a trace of silica. Evaporated to the consistency of syrup, and mixed with nitric acid, it deposited abundance of nitrate of urea. It also contained chloride of sodium, *urobenzoate* of soda, carbonate of soda, sulphate of potassa in large proportion, some sulphate of soda and carbonate of ammonia, and a trace of oxide of iron. No phosphoric salts or uric acid. (CHEVREUL.)

The urine of the *cow* contains a large relative proportion of urea and of hippuric (or *urobenzoic*) acid, and exposed to air, deposits small crystals of carbonate of lime and carbonate of magnesia.

Urinary calculi are not unfrequent in some of the above and other animals. They vary considerably in composition. Carbonate of lime, carbonate of magnesia, phosphate of lime, and ammonio-magnesian phosphate, are common ingredients; they also often contain a considerable proportion of a peculiar animal matter, of a resinous or fatty character. Oxalate of lime has been detected in the calculus of the rat; and in a calculus from a dog, Lassaigne found a substance which he terms *cystin*, or *cystic oxide*.

§ VI. SOFT SOLIDS OF ANIMALS. SKIN. GELATIN. MUSCLE, &c.

THE skin of animals consists of an exterior covering, the *epidermis*, or *cuticle*, under which is a thin stratum of a peculiar substance, called by anatomists *rete mucosum*, which lies immediately upon the *cutis*, *corium*, *dermis*, or *true skin*.

The *epidermis* varies in thickness on different parts of the body; it is little prone to decomposition, insoluble in water, in alcohol, and in dilute acids. Concentrated nitric and sulphuric acid soften and ultimately dissolve it. The caustic fixed alkalis dissolve it, even when considerably diluted, but not the carbonated alkalis. It is stained by several substances, so far indelibly that the colour remains till the cuticle peels off. It does not combine with tannin. Corns, and similar indurations, resemble the epidermis in their general chemical characters: and horn, hoof, nails, claws, tortoise-shell, hair, wool, feathers, and scales, may be regarded as modifications of it. All these substances partake more or less of the character of coagulated and dry albumen, and Mr. Hatchett's researches have shown, that the analogies between them are in many cases only broken by the presence of foreign substances.

The general colour of the surface of the body resides in the *rete mucosum*, the tint of which is much dependent upon the influence of light: the black skin of the African, the brown of the Asiatic and American, and the pinkish-white of the European, derive their colour from this peculiar secretion deposited between the *cutis* and *cuticle*; the nature of this substance has not been chemically investigated, but it has been ascertained in regard to the *black* of the negro, that it admits of being bleached by chlorine.

The *cutis*, or true skin, is of a fibrous texture, and when boiled in water is to a great extent soluble, leaving the vascular and nervous filaments which pervade it; the solution, when slowly evaporated, leaves a peculiar animal principle termed *gelatin*.

GELATIN is colourless, semi-transparent, and nearly tasteless. It is softened by long-continued immersion in cold water: in hot water it readily dissolves, and forms a solution of a slightly-opalescent appearance, which, if sufficiently concentrated, concretes on cooling into the tremulous mass usually called *jelly*, and which is easily soluble in water; when dried in a gentle heat, it acquires its original appearance, and is as soluble as before. According to Dr. Bostock, 1 part of *isinglass* dissolved in 100 of water gelatinizes on cooling; but in 150 of water it does not concreate. (NICHOLSON'S *Jour.*, xi. and xiv.) When *dry*, gelatin undergoes no change, but its *solution* soon becomes mouldy and putrescent. Submitted to the action of heat, it affords the usual products of animal substances.

Gelatin is readily soluble in diluted acids and alkaline solutions. (HATCHETT, *Phil. Trans.*, 1800.) Its aqueous solution is not affected by solution of corrosive sublimate, and few of the metallic salts occasion any precipitate in it. Chlorine passed through it occasions a white elastic matter to separate, which is not soluble in water, and which in some properties resembles albumen. Gelatin is insoluble in alcohol and ether, but alcohol does not form a precipitate in its aqueous solution. Solution of tannin occasions a white precipitate in solution of gelatin; and hence, vegetable astringents, such as infusion of galls or of oak-bark, are generally employed as tests for its presence. One part of dry gelatin, such for instance as isinglass, may be detected in 5000 of water by a strong infusion of galls: this precipitate when dried at 212° consists of about 60 gelatin + 40 tannin. But as tannin precipitates albumen, it cannot be relied on as an unequivocal test, unless we previously ascertain the non-existence of albumen by corrosive sublimate. (BOSTOCK, *Nicholson's Journal*, xiv. and xxi.) Mr. E. Davy recommends sulphate of platinum as a very delicate test of gelatin, with which it forms a brown insoluble compound, in solutions too weak to be affected by vegetable astringents. (*Phil. Trans.*, 1820, p. 119.) This is certainly a very delicate test; and is not affected by albumen.

The action of sulphuric acid upon gelatin has been investigated by Braconnot. Twelve parts of powdered *glue*, and 24 of sulphuric acid, were left together for 24 hours; about 60 parts of water were then added, and the whole boiled for 5 hours, adding water at intervals; the solution was then saturated with chalk, filtered, and suffered to evapo-

rate spontaneously. In a month, crystals were deposited, which, being purified by solution and a second crystallization, much resembled sugar of milk, though they differed from that substance in affording a peculiar acid, called by Braconnot *Nitro-saccharine acid*, when acted upon by nitric acid. (*Ann. de Ch. et Ph.*, xiii.)

The dilute acids are excellent solvents of gelatin, especially the acetic; these solutions do not gelatinize, but the gelatin is not decomposed, and reappears with its former properties on evaporating the acid, or abstracting it by an alkali or other base. The caustic alkalis do not materially affect gelatin, but they sometimes render its solutions turbid by decomposing phosphate of lime, which is often contained in it, and which is soluble, to a considerable extent, in solution of gelatin. The equivalent of gelatin has not been accurately determined, in consequence of the indefinite character of its combinations, but calculated in reference to the single atom of nitrogen, its composition may be represented as follows* :—

					Gay Lussac and Thenard.	
Carbon	7	. . .	42	. . .	48.28	47.881
Hydrogen	7	. . .	7	. . .	8.04	7.914
Oxygen	3	. . .	24	. . .	27.59	27.207
Nitrogen	1	. . .	14	. . .	16.09	16.998
<hr/>					<hr/>	
Gelatin	1		87		100.0	100.000

The different kinds of gelatin differ considerably in viscosity. Mr. Hatchett has remarked that the gelatin obtained from skins possesses a degree of viscosity inversely as their softness or flexibility; the most adhesive kinds of gelatin, too, are less easily soluble in water than those which are less tenacious. The principal varieties of gelatin in common use are:

a, Glue, which is prepared from the clippings of hides, hoofs, &c., obtained at the tan yard; these are first washed in lime water, and afterwards boiled and skimmed; the whole is then strained through baskets, and gently evaporated to a due consistency; afterwards it is cooled in wooden moulds, cut into slices, and dried upon coarse net work. Good glue is of a semi-transparent and deep-brown colour, and free from clouds and spots. When used it should be broken into pieces, and steeped for about 24 hours in cold water, by which it softens and swells; the soaked pieces may then be melted over a gentle fire, or in a water bath, and in that state applied to the wood by a stiff brush. Glue will not harden in a freezing temperature, the adhesion depending on the evaporation of its superfluous water.

b, Size is less adhesive than glue, and is obtained from parchment-shavings, fish skin, and several animal membranes. It is employed by

* "Gelatin may be considered as the least perfect kind of albuminous matter existing in animal bodies, intermediate, as it were, between the saccharine principle of plants, and thoroughly developed albumen. Indeed, gelatin in animals may be said to be the counter-

part of the saccharine principles of plants, it being distinguished from all other animal substances by its ready convertibility into a sort of sugar, by a process similar to that by which starch may be so converted." (PROUT.)

bookbinders, paperhangers, and painters in distemper, and is sometimes mixed with flour, gum, &c.

c, Isinglass is prepared from certain parts of the entrails of several fish; the best is derived from the sturgeon, and is almost exclusively prepared in Russia. It should be free from taste and smell, and entirely soluble in warm water, which is seldom the case, in consequence of the presence of some albuminous parts. When the jelly of isinglass is concentrated by evaporation and carefully dried, it forms a very choice kind of glue.

Berzelius, and some other chemists, regard gelatin as a *product*, and as in no case pre-existing in the textures whence it is obtained; they consider it as *formed by the action of heat on cellular membrane*, and hence all parts of the body in which cellular membrane exists, may yield gelatin by the continuous action of boiling water; the skin, being condensed cellular membrane, is particularly susceptible of this change; when gelatin is obtained by the action of acids, and without the intervention of heat, it is supposed that they also give rise to its formation. It is certain that, by long boiling, some animal substances are apparently converted into gelatin, in which its pre-existence cannot be demonstrated, and it sometimes seems to be more abundantly formed in this way at temperatures somewhat above the boiling point of water, than at 212° . It is, perhaps, in favour of this opinion, that gelatin is never found (except, perhaps, in the urine) in the natural fluids, or secretions of the body; it was once supposed to exist in the blood, but this has been disproved. Berzelius compares this production of gelatin to that of sugar from gum and starch. L. Gmelin found that a solution of gelatin, sealed hermetically in a glass tube, and exposed, for some weeks, to a boiling temperature, acquired a brown colour, lost its power of gelatinizing, and left a viscid residue on evaporation.

LEATHER is a compound of gelatin and tannin, formed by steeping the skins of animals in the infusions of certain barks, or other *vegetable astringents*. The skins are previously prepared by soaking in lime-water, which renders the cuticle and hair easily separable, and are afterwards softened by allowing them to enter into a degree of putrefaction, or occasionally by the action of acids. In this state they are submitted to the action of infusion of oak bark, or other astringent vegetable matter, the strength of which is gradually increased until a complete combination has taken place, which is known by the leather being of an uniform brown colour throughout; whereas, in imperfectly tanned leather, a white streak is perceptible in the centre. A portion of extractive matter, and occasionally other substances, enter into the composition of leather. Davy found the increase of weight in the skin to vary with the tanning material; thus 100 parts of calf skin tanned in concentrated infusion of galls increased in weight 64 parts; in a concentrated infusion of oak-bark 34 parts; in a weak infusion 17 parts; in concentrated infusion of willow bark 34 parts, and in a weak infusion 15 parts; and lastly, in a solution of catechu 19 parts.

Tanned leather is made by impregnating the skin, duly prepared by washing in potash liquor, with a solution of alum and common salt; it

is afterwards trodden in a mixture of yolk of eggs and water. The alum and salt re-act on each other so as to produce sulphate of soda and chloride of aluminum; the latter salt combines with the skin. White glove leather is thus prepared.

Wash leather is another important manufacture; in this the skin, after having been prepared and softened, is imbued with oil, and afterwards subjected to a weak alkaline solution.

Curried leather is made by besmearing the skin, or leather, while yet moist, with common oil, which, as the humidity evaporates, penetrates into the pores of the skin, giving it a peculiar suppleness, and making it, to a considerable extent, waterproof. As familiar examples of these processes, the thick sole leather for shoes and boots is *tanned*; the upper leather is *tanned* and *curried*; the white leather for gloves is *tawed*; and fine Turkey leather is *tawed*, and afterwards slightly *tanned*. (AIKIN'S Dictionary, Art. LEATHER.)

MUSCLE.—The muscle, or flesh of animals, is a complex texture, in which the muscular *fibre* is conjoined with cellular membrane, nerves and vessels, fat, and various fluids. On digesting muscular flesh in repeated portions of cold water, albumen, saline substances, and colouring and extractive matters are taken up; on heating the solution, the albumen is coagulated, and on evaporating the remainder in a water bath, a coloured extract remains, from which alcohol abstracts osmazome* and small quantities of saline matter (lactates?) and leaves a portion of extractive and salts insoluble in alcohol. When the part of the muscular fibre which is no longer acted on by cold water, is digested in hot water, its cellular substance is removed in the form of *gelatin*, and fatty matter separates. The insoluble residue is now little else than *fibrin*, and, when dried, presents the characters of that substance as it is above described amongst the ingredients of the blood. When any of the lean, muscular parts of animals are carefully dried, they lose greatly in weight by the evaporation of water; the residue, composed chiefly of albumen, fibrin, and cellular substance or gelatin, may be regarded as the real nutritive matters as articles of food, and it is curious that their relative proportions are not very dissimilar in quadrupeds, birds, and fishes, as shown in the following table. The water was determined by evaporation in vacuo, or at a temperature below 212°.

100 parts of Muscle of	Water.	Albumen or Fibrin.	Gelatin.	Total of Nutritive Matter.
Beef . .	74 . .	20 . .	6 . .	26
Veal . .	75 . .	19 . .	6 . .	25
Mutton .	71 . .	22 . .	7 . .	29
Pork . .	76 . .	19 . .	5 . .	24
Chicken	73 . .	20 . .	7 . .	27
Cod . .	79 . .	14 . .	7 . .	21
Haddock	82 . .	13 . .	5 . .	18
Sole . .	79 . .	15 . .	6 . .	21

* Osmazome, (from *οσμη*, *odour*, and *ζωμός*, *broth*,) is that product upon which the peculiar odour of broth or soup, and of dressed meat, depends; it is

of a yellowish-brown colour, soluble at all temperatures in water and in alcohol, and yields a precipitate with infusion of galls, but does not gelatinize.

It is commonly supposed that the flesh of young animals is much more abundant in gelatin than that of old ones, but the fact appears to be, that it is merely more soluble and more easily extracted by boiling, and in all cases where it is wished to remove from muscle the whole of the jelly, simmering at a temperature from 100° to 120° should be preferred to boiling, because by a temperature of 212° , the albumen is so firmly coagulated as to envelop the gelatin, and protect it from the solvent power of the water.

The action of sulphuric acid on muscle has been described by Braconnot: 30 parts of beef fibre, acted on by as much sulphuric acid, yielded a portion of fat, and on diluting the acid mixture, and saturating with chalk, filtering, and evaporating, a substance, tasting like osmazome, was obtained, which was often boiled in different portions of alcohol: the alcoholic solutions, on cooling, deposited a peculiar white pulverulent matter, which Braconnot calls *leucine*, and which, acted upon by nitric acid, affords a crystallizable *nitroleucic acid*. (*Ann. de Ch. et Ph.*, xiii. 118.) See BLOOD.

HAIR, as already stated, consists chiefly of a substance having the properties of coagulated albumen, and analogous in that respect to the cuticle; but hair also yields more or less gelatin when boiled with water, and the soft silky hair, which easily loses its curl, and is very susceptible of changes in the humidity of the atmosphere, yields gelatin more readily than that which is harsh, strong, and elastic. (HATCHETT, *Phil. Trans.*, 1800.) Vauquelin also discovered in hair two kinds of oil; the one white, and existing in all hair; the other coloured, yellow from red hair, and dark coloured when obtained from dark hair. Black hair also contains iron and sulphur. He supposes that where hair has become suddenly gray, the effect is produced by the evolution of acid matter, which has destroyed the colour of the oil.

MEMBRANES, LIGAMENTS, TENDONS, and some other similar textures, differ from *horn*, and from *indurated cuticle*, and also in some respects from *cartilage*, properly so called, by yielding gelatin when boiled.

§ VII. ANIMAL FAT.

IN its general characters and composition, the fat and oil of animals resembles that of vegetables; it is of various degrees of consistency, and contains stearin, margarin, and elain, in varying proportions; the action of alkalis upon these substances, and the properties of the acids and compounds thence resulting, are also in all respects similar to those of the vegetable oils, under the history of which much respecting the animal oils has been necessarily anticipated (p. 1128). The different degrees of consistency of these fats are seen in *tallow*, *lard*, and *oil*; when pure, they have, for the most part, little taste or smell; but by keeping, they become rancid and somewhat sour. The products of their combustion and destructive distillation also agree with those of vegetable oils, provided they are free from *cellular*, or as it is here called *adipose membrane*, from which they may be separated by cutting them, if necessary, into small pieces, and boiling them in water; the fat separates and floats upon

the surface, where it concretes on cooling; the foreign matters sink, or are dissolved in the water. For our knowledge of the principal characters of these substances, we are indebted, as already stated, to the laborious accuracy of Chevreul. I shall only here advert to such properties of these fats and oils as have not been above detailed, or to such of them as present distinctive peculiarities.

HUMAN FAT is soft, yellowish, inodorous, and varies a little in different parts of the body; that from the region of the kidneys, when fused, begins to concrete at 76° , and is solid at 64° . It is soluble in 40 parts of boiling alcohol of 0.821, and on cooling, the solution deposits *stearin*, which, after having been pressed between folds of blotting paper at 78° , is colourless, fusible at 122° , and may be cooled to 106° before it begins to congeal; its temperature then rises to 120° from the evolution of latent heat. 100 parts of boiling anhydrous alcohol dissolve 21.5 of this *stearin*, of which the greater part separates, on cooling, in acicular crystals. The *elain* of human fat is a colourless, inodorous oil, which retains its fluidity at 40° ; its specific gravity is 0.913 at 60° ; it has a sweetish taste. 100 parts of boiling alcohol dissolve 123 of this *elain*, and the solution becomes turbid when it has cooled to 170° .

HOGS' LARD is soft, white, and fusible between 78° and 86° . Its specific gravity at 60° is ≈ 0.938 , and at $120^{\circ} = 0.891$. When subjected to powerful and continued pressure at 42° , between folds of bibulous paper, it yields, according to Braconnot, 0.62 of its weight of a colourless *elain*, the specific gravity of which, according to Chevreul, is 0.915. 100 parts of boiling alcohol dissolve 123 of this *elain*, and the solution begins to grow turbid at 144° . The residuary *stearin* (0.38) is inodorous, dry, and granular; when fused, it remains liquid till its temperature sinks to 100° ; on congealing, it rises to 109° . When hogs' lard has become yellow and rancid by exposure to air, it reddens litmus, and contains a volatile acid resembling *caproic acid* (p. 1356).

Ox FAT, after fusion, begins to congeal at 98° , and the temperature then rises to 102° . It is soluble in 40 parts of boiling alcohol of 0.821, and contains about three-fourths its weight of *stearin*, which is hard, white, and of a granular crystalline texture; it does not fuse below 112° , and then may be cooled to 102° , when on congealing it rises to 112° . It is translucent, and not greasy, and burns like white wax. 100 parts of anhydrous alcohol dissolve 15.48 of this *stearin*; when saponified, it yields 0.951 of adipose acids. The *elain* of this fat is colourless, and nearly inodorous: its specific gravity 0.913. 100 parts of boiling anhydrous alcohol dissolve 123.4, and it yields by saponification 0.966 of fat acids.

After the hair and hoofs have been removed from the feet of oxen, they yield, when boiled with water, a peculiar fatty matter, called *neat's-foot oil*: it is not subject to rancidity, and remains fluid at 32° . After part of its *stearin* has been abstracted, it is used for various purposes, and among them, for oiling steeple clocks, which require, in consequence of the cold to which they are exposed, an oil not liable to solidify.

MUTTON FAT, in external characters, resembles that of oxen, but it is whiter, and acquires a peculiar odour by exposure to air. When melted, it sometimes begins to congeal at 98° , and the temperature then rises to 102° , or it congeals at 104° , and then its temperature only rises to 105° or 106° . It is soluble in 44 parts of boiling alcohol of 0.821. Its *stearin* is white and translucent, and very imperfectly crystalline after fusion. 100 parts of boiling anhydrous alcohol dissolve 16.09 parts. Its *elain* is colourless; specific gravity = 0.913. 100 parts of anhydrous alcohol, at 168° , dissolve 80 parts*.

These two fats are highly important, from their application to the manufacture of *soap* and of *candles*: and of late the *stearin* has been employed for the latter purpose, which, fused with from one-fourth to one-eighth part of wax, yields a compound very little inferior to wax, of which the best and genuine *composition candles* are made. Under this term a variety of very inferior articles are sold at comparatively low prices, which have tended to bring this important manufacture into some degree of discredit; and the art of preparing *stearin* by cheap, and at the same time effective processes, is not as yet very perfect; but this application of it is daily improving, and promises to place the art of making candles not low upon the list of those which have been enlightened and improved by the labours of the chemist. (See page 1137.)

GOATS' FAT is characterized by its peculiar capreous odour, arising from its containing a peculiar fat, which Chevreul has termed *hircin*, and which, on the separation of its tallow into *stearin* and *elain*, accompanies the latter, and cannot be perfectly separated from it. During the saponification of its *elain*, a liquid acid of a strong goaty odour is formed: it may be obtained by saponifying 4 parts of goat fat with 1 of hydrate of potassa and 4 of water, diluting the soap with more water, and decomposing it by phosphoric or tartaric acid, washing the evolved fat acids, and distilling the sour water and washings; if a drop of the distilled product, evaporated upon a platinum leaf, leaves any residue, it must be redistilled; the product is then to be saturated by hydrated baryta, evaporated to dryness, and decomposed by distillation with equal parts of sulphuric acid and water: the *hircic acid* then passes over in the form of a colourless volatile oil.

Hircic Acid has a capreous and acetic odour, reddens litmus, and dissolves difficultly in water, and easily in alcohol. It forms distinct salts with the bases; *hircate of ammonia* is peculiarly odorous; *hircate of potassa* is deliquescent; *hyrcate of baryta* is difficultly soluble.

TRAIN OIL. WHALE OIL.—Common *whale oil* has a specific gravity = 0.927 at 68° ; at 32° it deposits *stearin*, and the remaining *oil* is then soluble in 0.82 of its weight of absolute alcohol at 168° . It is easily

* When mutton or beef suet is distilled, and the product washed with hot water, it dissolves a peculiar acid, which is Thenard's *sebacic* or *sebic* acid. The solution is precipitated by acetate of lead, and the resulting *sebate of lead* decomposed by its equivalent of sulphuric acid; the *sebic acid* is then purified by

crystallization; it forms colourless, fusible, and volatile acicular crystals; more soluble in hot than in cold water, and very soluble in alcohol. The *sebates of ammonia, potassa, and soda*, are soluble; those of *lead, mercury, and silver*, are insoluble.

saponified, yielding a brown soluble soap, which, decomposed by tartaric acid, affords fat acids and glycerin, together with traces of *phocenic acid*. The *stearin* of train oil congeals, after fusion, at between 70° and 80° . It dissolves in 1.8 parts of boiling anhydrous alcohol, from which it crystallizes on cooling, leaving a brown mother liquor.

SPERMACETI OIL.—The oil of the spermaceti whale is more pure, and burns more perfectly and more brilliantly in lamps than common whale oil; it deposits, as it cools after the death of the animal, a crystalline fatty substance, called *spermaceti*, which is purified by pressure, and boiling in weak solution of potassa; it is then washed, fused in boiling water, and cast into blocks or cakes, which exhibit a beautiful lamellar crystalline texture, especially when the interior liquid part is suffered to run out of the exterior concrete case. It has a greasy feel. Its specific gravity is about 0.94; it fuses at 112° . 100 parts of boiling alcohol of 0.821 dissolve 3.5 parts, of which 0.9 fall on cooling. Its solution in hot ether congeals on cooling. It dissolves in the hot oils. When common spermaceti is triturated with alcohol, a little oily matter is abstracted; and when the whole is removed, the residuary pure spermaceti has been termed by Chevreul *cetin*.

CETIN fuses at 120° . 100 parts of boiling absolute alcohol dissolve 15.8 of cetin, but alcohol, of 0.831, only 3 parts; the greater part separates on cooling in pearly scales. Acids act upon it as on other fats. It is difficultly saponifiable by the hydrated alkalis. Digested for several days between 120° and 190° , with a solution of caustic potassa, in twice its weight of water, it is at length converted into a peculiar soap, containing margarate and oleate of potassa, together with an unsaponified fat, which Chevreul terms *ethal*. On decomposing this soap by an acid, ethal, and oleic and margaric acids separate, amounting together to 101.6 parts from 100 of cetin; of this 60.96 parts consist of fat acids, and 40.64 of ethal: no glycerine is produced, but 0.9 of a yellowish extractive matter; nor is any volatile acid formed.

Chevreul, Saussure, and Berard have analyzed cetin and ordinary spermaceti, and Dr. Ure spermaceti oil, with the following results:—

	<i>Cetin.</i> Chevreul.	<i>Spermaceti.</i> Berard.	<i>Spermaceti.</i> De Saussure.	<i>Spermaceti Oil.</i> Ure.
Carbon .	81.660 . .	79.5 . .	75.474 . .	78.00
Hydrogen	12.862 . .	11.6 . .	12.795 . .	11.80
Oxygen .	5.478 . .	8.9 . .	11.377 . .	10.20

ETHAL is obtained by saturating the fat acids resulting from the decomposition of spermaceti soap with hydrated baryta, washing away all excess of baryta, drying the residue, and digesting it in cold alcohol or ether, which dissolves the ethal and leaves barytic soap. The ethal remains, on distilling off the alcohol, in the form of a solid transparent crystalline fat. Ethal may also be obtained by adding 1 part of caustic potassa, in small fragments, to 2 parts of fused spermaceti, and stirring the mixture till the combination is complete; a solid soap is thus formed, which may be decomposed by slight excess of hydrochloric acid, when the ethal and free acids separate, and form, when gently heated, an oily layer upon the surface, which is to be poured off and again saponified, in

order effectually to decompose all remaining spermaceti, decomposed by hydrochloric acid as before, and the ethal and acids poured off and mixed with excess of slaked quicklime: the mixture of calcareous soaps and ethal, thus obtained, is digested in alcohol, which takes up the ethal and leaves it on distillation: it may be finally purified by solution in ether, and subsequent evaporation or distillation. It is tasteless and inodorous, and concretes, when fused alone, at 118° , but if fused with water, at 124° . It is volatile when distilled either alone or with water, and in this way it may be purified; it burns like wax. It dissolves in all proportions in alcohol of 0.812 at 128° , and separates, on cooling, in lamellar crystals. It is decomposed when heated with sulphuric and nitric acid. It does not combine with caustic potassa, when pure, but when mixed with soap it forms a milky fluid, which leaves, upon a filter, a mixture of ethal, with margarate and oleate of potassa, exactly resembling hydrated alumina. According to Chevreul's analysis, ethal consists of

					Chevreul.				
Carbon	16	96	79.3	79.7660	} = { Etherine 4 . 112 Water . 1 . 9				
Hydrogen	17	17	14.1	13.9452					
Oxygen	1	8	6.6	6.2888					
Ethal	1	121	100.0	100.0000	Ethal	1	121		

CETENE.—By distilling ethal with pure phosphoric acid, Dumas and Peligot succeeded in abstracting its water, and obtaining its hydrocarbon in a free state; it passed over in the form of an oily liquid more volatile than ethal, and yielding a vapour of the density of 7.846, whence they infer that it is a distinct form of hydrocarbon, consisting of ($16h + 16car$), so that 1 volume of its vapour would include 16 volumes of hydrogen and 8 volumes of carbon vapour. To this compound they have given the name of *Cetene*. (*Ann. de Ch. et Ph.*, lxii. 1.) Its equivalent is 112; and ethal is a *monohydrate of cetene*, or $112 + 9 = 121$.

Cetene is a colourless, tasteless liquid, leaving a greasy stain on paper, and of an oily aspect: it boils at 528° (275° Cent.), and distils unaltered; it is insoluble in water, very soluble in alcohol and ether, and inactive upon test papers. It burns with a pure white flame. As it does not congeal, and is apparently unchanged by exposure to air, it would probably furnish a valuable substitute for oil, as applied to watches and clocks.

Sulphocetic Acid.—When ethal and sulphuric acid are heated in a water bath, they combine, and on dissolving the product in alcohol and saturating the solution with an alcoholic solution of potassa, sulphate of potassa is deposited, and sulphocetate of potassa and ethal remain dissolved: on filtering and evaporating the liquid, crystals are obtained, which must be redissolved in absolute alcohol, to separate adhering sulphate of potassa, and recrystallized: this product is then triturated with sulphuric ether, to remove any remaining ethal, and pure sulphocetate of potassa remains. It is a white nacreous salt.

According to Dumas and Peligot, an atom of spermaceti is so constituted as to be represented by 2 atoms of *margarate of cetene* + 1 atom of *oleate of cetene*.

PORPOISE OIL.—The oil of the *Delphinus phocaena*, and *Delphinus globiceps*, has been examined by Chevreul. When saponified it yields

a peculiar fat acid, which has been termed *phocenic*, or *delphinic acid*. This acid is best obtained from that portion of porpoise oil which remains dissolved in cold alcohol of 0·825. It is saponified, and a *phocenate of baryta* formed, 100 parts of which are decomposed by 205 of phosphoric acid, of 1·12 specific gravity, or by 23·4 parts of sulphuric acid, diluted with twice its weight of water, when nearly the whole of the phocenic acid separates. This acid exists in spermaceti, and in the berries of the *Viburnum opulus*.

Phocenic acid resembles a volatile oil, retaining its fluidity at 15°; although its boiling point is above 212°, it volatilizes in the air; it has a rank and acetic odour and acrid taste. Its specific gravity is 0·932 at 77°; water at 88° only dissolves an eighteenth part of its weight; alcohol of 0·795 takes it up in all proportions. Anhydrous phocenic acid consists, according to Chevreul's analysis, of

Carbon	20	. .	120	. .	65·6
Hydrogen	15	. .	15	. .	8·1
Oxygen	6	. .	48	. .	26·3
<hr/>					
Anhydrous phocenic acid	1		183		100·0

It appears, however, that in the neutral *phocenates*, the oxygen in the acid is to that in the base as 3 to 1, so that the above equivalent is doubled in reference to that of the bases. When the phocenates are heated, they exhale an aromatic odour, and yield, on distillation, an oily liquid, insoluble in potassa. The *phocenates of potassa*, *soda*, and *strontia* are deliquescent; *phocenate of baryta* yields efflorescent crystals, soluble in their weight of water. *Phocenate of lead* is soluble, but during the evaporation of its solution passes into a difficultly-soluble subsalt.

Phocanine is the term applied by Chevreul to that part of the oil which yields phocenic acid, and which is separated, by boiling alcohol, from the common fats.

FAT OF BIRDS.—*Goose fat* is colourless, and of a peculiar taste and odour; when fused, it congeals at 80° to a buttery consistence; subjected to pressure at 30°, it yields 0·68 *elain*, and 0·32 *stearin*, fusible at 112°. *Ducks' fat* fuses at 76°, and yields 72 *elain* and 28 *stearin*, fusible at 120°. *Turkeys' fat* yields 74 *elain* and 26 *stearin*, fusible at 112°.

FAT OF INSECTS.—Many insects contain more or less fat, but its peculiarities have been but little examined. The fatty matter of *cochineal* (*Coccus cacti*) has been examined by Pelletier and Caventou. (*Ann. de Ch. et Ph.*, viii. 271.) It is obtained by digesting cochineal in ether, evaporating, and dissolving the residue in hot anhydrous alcohol, which, on cooling, deposits the fat; this solution must be repeated till it is colourless. The fat of the *Coccus polonicus* crystallizes like spermaceti. *Cantharides* also contain a fatty matter, and an acrid principle, or *cantharadin*. If the watery extract of these insects be digested in alcohol, a tincture is obtained, which, by slow evaporation, yields a resinous residue; if this be digested in ether, it forms a yellow solution; by spontaneous evaporation it deposits crystalline plates, which may be freed from some adhering colour by alcohol; they resemble spermaceti in appearance, and are soluble in boiling alcohol, but precipitate as it cools.

They are insoluble in water. Besides this peculiar principle, cantharides contain a green inert oil, soluble in alcohol; a black matter, insoluble in alcohol, but soluble in water; a yellow substance, soluble in both; a considerable portion of uric acid; a little acetic acid, and phosphates of lime and magnesia.

Eggs*.—The yolk of the hen's egg contains about 30 per cent. of oil. When the yolk is digested in alcohol a yellow solution is obtained, which deposits a crystalline fat, and leaves, on evaporation, a yellow viscid oil, which easily becomes rancid. The insoluble residue is white and pulverulent, and consists chiefly of albumen, but contains a considerable portion of phosphorus in some peculiar state of combination.

AMBERGRIS, which is a concretion from the intestines of the spermaceti whale, also contains a considerable portion of fatty matter, amounting, in some specimens, to 60 per cent., which, according to Chevreul, resembles cholesterine. Pelletier and Caventou have given it the name of *Ambreine*, and it is stated to be convertible by nitric acid into a peculiar body, which they have called *ambreic acid*. It is only found in the unhealthy animal. (HOME'S *Lectures on Comparative Anatomy*, vol. i., p. 470.) Benzoic acid has been found in some specimens of ambergris; in others, equally genuine, there are no traces of it.

Musk, *castor*, and *civet*, exclusive of their peculiar and odorous principles, contain distinct species of fat.

INTESTINAL CONCRETIONS sometimes bear a resemblance to gallstones, but they often contain peculiar substances, or are formed upon extraneous nuclei. Dr. Ure has described one resembling ambergris. (*Dict.*, Art. INTESTINAL CONCRETIONS.) The Oriental *Bezoar stones* are also apparently of this description. Intestinal concretions are not uncommonly formed upon fruit stones, and seem to be peculiarly frequent where the diet has consisted of oatmeal. One examined by

* The changes which the egg undergoes during incubation, have been investigated by Dr. Prout. (*Phil. Trans.*, 1822.) New-laid eggs are somewhat heavier than water, but gradually become lighter by the evaporation of water and substitution of air, through the shell. When an ordinary sized egg is boiled in water it loses about three-tenths of a grain, consisting of the sulphates, phosphates, and carbonates of lime and magnesia, animal matter, and free alkali. Of an egg which weighs 1000 grains, 106.9 parts constitute the *shell*, 604.2 the *white*, and 288.9 the *yolk*. The shell contains about 2 per cent. of animal matter, 1 of phosphate of lime and magnesia, and the residue is carbonate of lime with a trace of carbonate of magnesia. The phosphorus contained in the yolk yields the phosphoric acid requisite for the bones of the chick, but the source of the lime

for that purpose is not obvious; Dr. Prout could not detect it in the soft parts of the egg, and there is no apparent vascular connexion between the chick and the shell.

The eggs or roe of fish contain also a considerable proportion of oil. The roe of the sturgeon, which, when salted, is known under the name of *caviar*, contains 6.2 albumen; 4.3 fat; 24.3 coagulated albumen and membrane; 6.7 common salt; 0.5 phosphate of lime and oxide of iron; 0.58 water. (JOHN.) The *melt*, or soft roe of the male fish, resembles in composition the liver or the brain; it yields an emulsion with water, containing fat and albumen, and, when incinerated, much phosphoric acid is found in the coal. The liver of many fish is abundant in a peculiar kind of oil; that of the *cod-fish* yields it in considerable quantity.

Mr. Children (*Phil. Trans.*, 1822) consisted of animal matter, chiefly gelatine, 25·20; resin 3·90; ammonio-magnesian phosphate 5·16; phosphate of lime 45·34; vegetable fibre 20·30.

Alvine calculi have sometimes a peculiar softness upon the surface resembling velvet. One of these was found by Dr. Wollaston to consist of extremely minute vegetable fibres, or short needles, pointed at both ends, which he immediately conjectured to arise from some kind of food. For some time, however, he failed in his attempts to trace this substance to its origin; but Mr. Clift, of the College of Surgeons, to whom the subject was mentioned in conversation, having put the question whether this fibrous substance might not proceed from oats, Dr. Wollaston was induced to examine the structure of this seed; and the result fully verified Mr. Clift's conjecture. In Dr. ALEXANDER MONRO'S *Morbid Anatomy of the Gullet*, mention is made of 42 alvine concretions collected by the author's father, which were examined by Dr. Thomson. Their structure (with one exception, similar in all) is described by Dr. Monro "as more or less porous, and somewhat like to dried sponge, and when examined by the aid of a magnifying glass, seems to be made up of a number of very small fibres intimately interwoven with each other, like those in a hat, or in chamois leather; and the interstices between the fibres are filled up with earthy matter." And he adds, "in the centre of the concretion, a *prune* or a *cherry stone*, or a small piece of bone, or a biliary calculus, is generally found."

BRAIN.—The substance of the brain, nerves, and spinal marrow, contains fat, together with albumen and phosphorus. When boiled in alcohol it furnishes a peculiar fatty matter, which the solution deposits as it cools, in brilliant scales. It requires a higher temperature than that of boiling water for its fusion, and appears, in many respects, analogous to cholesterine. The same substance is often seen in the alcohol employed to preserve anatomical preparations of the brain and nerves.

According to Vauquelin, the *cerebral substance* consists of water 80·00, white fatty matter 4·53, red fatty matter 0·70, albumen 7·00, ozmazome 1·12, phosphorus 1·50, acids, salts, and sulphur 5·15. According to Couerbe, the crystalline fatty matter of the brain is partly *cholesterine*. He considers the proportion of phosphorus in the brain of persons of sound intellect to amount to from 2 to 2·5 per cent., but he asserts that this element is in deficiency in the brain of idiots, and in excess in that of maniacs; amounting in the former to not more than 1 to 1·5 per cent., but in the latter to as much as 3, 4, and even 4·5 per cent. If this statement be verified by extended inquiries, it appears to include a most important physiological fact.

A large concretion, weighing 54 grammes, of the size of a hen's egg, found in the right ventricle of the brain of an old horse, consisted of cholesterine 58, membrane and albuminous matter 39·5, subphosphate of lime 2·5. It produced no observable symptoms. (LASSAIGNE, *Ann. de Ch. et Ph.*, LXII. 222.)

CERUMEN, or the waxy secretion which lines the external tube of the ear, has been examined by Vauquelin, and more in detail by Berzelius. (*Thier-Chemie: Lehrbuch*, iv.) According to Vauquelin, it contains

0.625 of a brown, buttery oil, soluble in alcohol, 0.375 of an albuminoid substance, and a bitter extractive matter. According to Berzelius, it is a compound of a soft fat, with albumen and another peculiar principle, a yellow bitter extract soluble in alcohol, an extract soluble in water, with alkaline and calcareous lactates; but it contains no chloride, and no soluble phosphate.

§ VIII. SHELL AND BONE.

WE are indebted to Mr. Hatchett for two excellent dissertations on the chemical properties of these parts of animals, published in the *Philosophical Transactions* for 1799 and 1800. He has divided *shells* into two classes; the texture of the first is compact, brittle, and resembling porcelain; their surface is smooth, and they are often beautifully variegated. When exposed to a red heat they crackle, and lose the colour of their enamelled surface, emitting scarcely any smoke or smell. They dissolve in dilute hydrochloric acid with copious effervescence, and form a transparent solution, in which neither pure ammonia nor acetate of lead produces any precipitate, but carbonate of ammonia throws down carbonate of lime. Hence these, which are called *porcellaneous shells*, may be considered as composed of carbonate of lime, united to a very small portion of gelatine: most of the univalve shells, such as whelks, limpets, cowries, and many of the beautiful convoluted shells of tropical countries, belong to this class.

The second class, or *mother-of-pearl shells*, are tougher, glossy, and iridescent; they are mostly bivalves, and all the oyster and muscle species belong to it. When heated they exhale smoke and the smell of burned horn; immersed in hydrochloric acid, they only partially dissolve, and leave a series of cartilaginous layers, and an outer epidermis. Each membrane appears to have a corresponding stratum of carbonate of lime, the solution indicating no trace of any phosphate. The animal part is in some cases, as in mother-of-pearl, tough and indurated, and, when dried, becomes exactly like horn; in other instances, as in the bone of the cuttle fish, it appears in the form of delicate and tender membrane.

In both classes of shells, therefore, the hardening principle is carbonate of lime; in porcellaneous shells there is very little animal matter, which is gelatine; and in mother-of-pearl shells, it is albumen, and in larger quantities.

Pearls are exactly similar in composition to what is termed *mother-of-pearl*, in which Mr. Hatchett found carbonate of lime 66, albumen 24.

Corals or *Zoophytes*, according to Mr. Hatchett's researches, may be divided into four classes: 1. The first class resembles porcellaneous shells; they consist entirely of carbonate of lime, with a very minute quantity of gelatinous matter; of this the common white coral (*Madrepora virginea*) is an example. 2. The second consists of carbonate of lime, and a cartilaginous substance, and is therefore analogous to mother-of-pearl shell; to this class belong the *Madrepora ramea*, and *Madrepora fascicularis*. 3. The third class is composed of a cartilaginous matter, with carbonate and phosphate of lime; to this belongs the red coral. (*Gorgonia nobilis*.)

4. The fourth class contains sponges, composed almost entirely of animal matter (*Phil. Trans.*, 1800).

BONE AND IVORY, like the preceding substances, are essentially composed of soft and hard parts. When ground bone is digested in warm water, a portion of fat is first separated, and by long-continued ebullition, a solution which gelatinizes on cooling is obtained. If fresh bone be immersed in diluted hydrochloric acid, the fat, gelatine, and bony matter are dissolved, and a kind of skeleton of the bone remains in the form of a cartilaginous substance, which, when dried, exactly resembles horn. It appears, therefore, that the soft parts of bone are, *fat, gelatine, and albumen.*

The earthy salts, which constitute the hardening principle of bone, are phosphate and carbonate of lime, with a minute quantity of sulphate of lime, and traces of phosphate of magnesia. Fourcroy and Vauquelin obtained from *ox bones*, animal matter 51·0, phosphate of lime 37·7, carbonate of lime 10·0, phosphate of magnesia 1·3. According to Berzelius, 100 parts of dry *human bones* contain 33·3 animal matters, 51·04 phosphate of lime, 11·30 carbonate of lime, 2 fluete of lime, 1·16 phosphate of magnesia, soda, chloride of sodium, and water 1·2. Traces of alumina, silica, manganese, and iron, were discovered in bones by Fourcroy and Vauquelin, and of sulphate of lime by Hatchett.

The *enamel of teeth* is perfectly destitute of cartilage, and consists chiefly of phosphate of lime and a portion of gelatine. Mr. Pepys found its component parts, phosphate of lime 78, carbonate of lime 6, gelatine 16.

The same chemist has given the following as the composition of the teeth. (Fox, *On the Teeth.*)

	Roots of the Teeth.	Teeth of Adults.	First Teeth of Children.
Phosphate of lime	58	64	62
Carbonate of lime	4	6	6
Cartilage	28	20	20
Water and loss	10	10	12
	100	100	100

The difference between the structure and composition of the enamel and bone of teeth, is well illustrated in the teeth of some of those graminivorous animals, in which the enamel, instead of being external, alternates in layers with the bone: the section, for instance, of the elephant's tooth exhibits three distinct substances, namely, a hard and a softer bone, and an enamel; when steeped in dilute hydrochloric acid, the latter is entirely dissolved; the bony portions leave variable proportions of cartilage.

We have as yet but few accurate comparative analyses of the bones of different animals. In human bone carbonate of lime is much more abundant, according to Berzelius, than in that of the ox: the relative proportions of these salts also vary considerably in other cases, as is shown in the following analyses of the earthy residue of different bones, by De Barros. (BERZELIUS'S *Lehrbuch.*)

	Phosphate of Lime.	Carbonate of Lime.
Lion	95 0	2.5
Sheep	80 0	19.3
Hen	88.9	10.4
Frog	95.2	2.4
Fish	91.9	5.3

The bones of fish appear, in almost all cases, to contain much less earthy matter than those of quadrupeds or birds. According to Chevreul, the bones of the head of the cod contain, animal matter and moisture 43.94, phosphate of lime 47.96, carbonate of lime 5.50, phosphate of magnesia 2.00, soda-salts, chiefly chloride, 0.60. The bones of the *haddock* contain, according to Dumenil, animal matter 37.63, phosphate of lime 55.26, carbonate of lime 6.16, traces of soda, salts, and loss, 1.22.

The cartilaginous part of the bone is that which is first formed, as seen in the skeletons of young animals; and in the case of a bone being broken, the animal portion is first secreted, and it is gradually hardened by the deposition of the earthy salts, so as perfectly to reunite the fractured extremities; it is stated by Lassaigne, that in the newly-formed bone, phosphate of lime at first predominates; but that when the new portion is perfected, it contains the same relative proportions of phosphate and carbonate as those of the original bone.

The bones, including their animal matter, are the most durable portion of the animal fabric, hence the proposal of storing them up as occasional sources of nutriment; for not only is the cartilaginous portion unimpaired in bones which have been kept dry for many years, but it has even been found perfect in bones of apparently antediluvian origin. The best mode of extracting the nutritious part of the bone for human food consists in grinding it fine, and subjecting it with water to a heat of about 220°, in a digester; or the earthy part may be removed by hydrochloric acid. When dogs, and some other animals, are fed on bones, the nutritive portion is effectually abstracted by the gastric juice, and the excrement, in such cases, is almost entirely phosphate and carbonate of lime, forming the *Album Græcum* of old pharmacy.

When bones are submitted to destructive distillation, the gelatine and albumen which they contain is abundantly productive of ammonia; water and carbonic acid are also formed, and a portion of foetid empyreumatic oil. There remains in the vessel a quantity of charcoal mixed with the earthy substances, which is, in that state, called *ivory black*. It is employed as the basis of some black paints and varnishes, and when freed of phosphate of lime by digestion in dilute hydrochloric acid, is applicable to many useful purposes in the arts, as a variety of animal charcoal.

§ IX. ANIMAL FUNCTIONS.

CHEMISTRY has hitherto done little towards elucidating the *functions of animals*, and it is scarcely possible to describe the little that has been done, without such frequent reference to anatomical and physiological inquiries as would be irrelevant to the present work: I shall, therefore, only enumerate the principal chemical phenomena that have been experimentally illustrated, in relation to this subject.

Digestion is a process by which the food of animals is converted, by a series of successive changes, into *chyle*, and which, in conjunction with *respiration*, tends to the production of blood. The mechanism by which this important function is carried on differs considerably in the different classes of animals: the present remarks will relate chiefly to man, and to the carnivorous tribe.

The food of all living beings is necessarily of organic origin, some deriving it from animal, some from vegetable sources, and some from both. But all organic substances are not equally susceptible of digestion, and this is especially the case with those belonging to the vegetable kingdom; and as one of the functions of the stomach and intestines consists in separating the nutritive and digestible from the indigestible substances, those organs are generally more complicated and extended in graminivorous than in carnivorous animals. The most nutritive and digestible principles of vegetables, are those which include nitrogen as one of their elements, such as albumen, gluten, and perhaps a few varieties of extractive matter; they bear some resemblance, in this respect, to animal products. Yet it is also to this class that the most virulent poisons belong; so that the existence or non-existence of nitrogen is far from a criterion of their fitness or inaptitude for food. Starch, gum, and sugar, are also generally regarded as highly nutritive principles, and they are so in conjunction with the former, or with animal food; but these, and other substances destitute of nitrogen, are not alone capable of indefinitely supporting the life of graminivorous tribes; and it is doubtful how far graminivorous animals can continue to exist upon them. The experiments of Majendie, and of Tiedemann and Gmelin, upon these subjects, should be consulted; they seem to show the curious fact that no *single* substance is adapted to animal sustenance, for geese fed upon gum died on the sixteenth day, those fed upon starch on the twenty-fourth day, and those fed on boiled white of egg on the forty-sixth day: in all these cases they dwindled away, and died as if of starvation.

Woody fibre is generally regarded as indigestible, and many of its modifications, in their ordinary states, certainly are so, for they pass through the stomach and bowels unchanged; but when minutely divided, or modified by heat, or in the attenuated state in which lignin exists in certain roots and fruits, it probably is more or less digestible. Resins, and analogous substances insoluble in water, are also unfit for food. Vegetable acids, alcohol, certain aromatics, and oils, are rather to be considered as condiments and stimulants, and so far essential to digestion, than as contributing to the direct nutritive power of food. Among animal substances, hair, feathers, the shells of insects*, and a few other products, belong to the class of absolute indigestibles.

The food, duly masticated in the mouth, and blended with a considerable portion of saliva, is propelled into the stomach, where it soon undergoes a remarkable change, and, in the course of a few hours, is

* Odier has applied the term *Chitin*, (from *χίτων*, a coat of mail,) to the hard shells, and elytra of insects, or to the most insoluble parts: they would appear, however, from Mr. Hatchett's experiments, to be modifications of indurated albumen, analogous to scales, feathers, nail, horn, &c.

converted into an apparently homogenous pulpy mass, which has been termed *chyme*, and which has little or no resemblance to the original food. This very curious change is only referable to the operation of the *gastric juice*; the remarkable property of living substances to resist its action is curiously illustrated by the circumstance that the stomach itself, after death, is occasionally eaten into holes by it; it coagulates albuminous substances, and afterwards softens and dissolves the coagulum.

Although animals drink copiously with their food, the consistency of the chyme is not apparently much affected by it, and by the time that it reaches the right, or pyloric extremity of the stomach, the greater part of the liquid has disappeared. Sir Everard Home has shown that the liquids are removed by absorbents belonging principally to the left, or cardiac portion of the stomach, and that during digestion there is an imperfect division of the stomach into two cavities, by the contraction of the bands of muscular fibres about its centre. He has also shown that these liquids reach the kidneys, and pass off by urine; and was led to believe that the spleen was the channel of communication; an opinion, however, which his subsequent researches tended to disprove. (*Lectures on Comparative Anatomy*, p. 221.)

The chyme passes from the stomach into the small intestines, where it soon changes considerably in appearance; it becomes blended with bile, and is separated into two portions, one of which is white as milk, and is termed *chyle*; the other passes on to the large intestines, and is ultimately voided as excrementitious*. The chyle is absorbed by the *lacteals*, which terminate in the common trunk, called the *thoracic duct*; it is there mixed with variable proportions of lymph, and poured into the venous system. The *excrements of animals* have been examined by Berzelius (*Gehlen's Journ.*, vi.), by Vauquelin (*Ann. de Ch.*, xxix.), and by Thaer and Einhoff.

Chyle has been examined by several chemists, and their results are not widely different. During some physiological researches in which I assisted Sir B. Brodie, I had an opportunity of collecting it in considerable quantities in several carnivorous and graminivorous animals, and presented an account of some experiments upon it to the Royal Society. (*Phil. Trans.*, 1812.) Chyle is an opaque white fluid, having a sweetish saline taste; its specific gravity is inferior to that of the blood. It exhibits slight traces of alkaline matter when tested by infusion of violets; soon after removal from the thoracic duct, it gelatinizes spontaneously, and afterwards gradually separates into a firm yellowish-white coagulum, and a transparent colourless serum; so that, like the blood, it enjoys the property of spontaneous coagulation.

* The necessity of bile to the formation of chyle has been illustrated by Sir B. Brodie. (*Quarterly Journal*, O.S., xiv. 341.) When the choledoch duct was tied so as effectually to prevent the flow of bile into the intestine, no chyle was formed; the chymé appeared little altered; and the lacteals, instead of their usual milky fluid, contained a transparent fluid, consisting, apparently, of

lymph, and of the more fluid part of the chyme. Tiedemann and Gmelin assert, that under these circumstances chyle is formed; and Berzelius also says that chyle is formed, but that it is transparent because its oil is not saponified; but it must surely be difficult in these cases to distinguish between *transparent chyle* and certain modifications of lymph.

The *coagulum of chyle* possesses properties closely resembling those of the caseous portion of milk, and may hence be considered as a variety of albumen; the *serum of the chyle*, when heated, deposits a few flakes of albumen, and by evaporation to dryness affords a small proportion of a substance analogous to sugar of milk. Small portions of phosphate of lime, carbonate of soda, and common salt, may also be detected in the chyle. In these experiments I found no essential difference in the chyle of graminivorous and carnivorous animals; I examined it from the horse, the ass, the dog, and the cat; Dr. Marcet thinks that the former is less abundant in albumen than the latter. (THOMSON'S *Annals*, vol. vii.) From a comparative analysis of the chyle of two dogs, by Dr. Prout, of which one was fed on vegetable, and the other on animal food, the components were found to be as follow (*Ann. of Phil.*, xiii. 25):—

	Vegetable Food.	Animal Food.
Water	93·6	89·2
Fibrin	0·6	0·8
Incipient albumen ?	4·6	4·7
Albumen with a little red colouring matter	0·4	4·6
Sugar of milk	a trace	0·0
Oily matter	a trace	a trace
Saline matter	0·8	0·7
	100·0	100·0

There can be little doubt that the bile performs an important part in the change which the chyme suffers in the small intestines; it has been conjectured that its aqueous, and perhaps its alkaline, parts, are employed as components of chyle, while the albumino-resinous matter combines with the excrementitious portion, and tends to stimulate the intestinal canal towards promoting its propulsion. Whether the bile is absolutely necessary to the formation of chyle, is a question that has not been satisfactorily answered; but its importance is demonstrated by the emaciation that attends its deficiency, and by the disordered state of bowels that accompanies its imperfect secretion. Sir Everard Home, in his *Lecture on the Functions of the Lower Intestines*, (*Lectures*, p. 468,) has offered some curious facts connected with this subject, to which I refer the physiological reader. He is of opinion that, in the large intestines, a portion of the food unfit for chylication is, by a process not widely different from that above described, converted into fat, which is afterwards absorbed and conveyed to different parts of the body.

In chyle we cannot fail to observe an approximation to blood; it is deficient in colouring matter, and the albumen which it contains differs somewhat from that existing in the blood itself; it appears, therefore, that the albumen is perfected, and fibrin and colouring matter formed, in the process of circulation.

The difference between arterial and venous blood has been adverted to in a previous section: the former is of a florid red colour, and circulates in the arterial system; it is contained in the left ventricle of the heart, and thence carried by the *aorta*, and its ramifications, to every part of the body, tending to reproduction and secretion: it afterwards enters the veins which arise from the extremities of the arteries, and form accompanying branches, and trunks, ultimately uniting in the *venæ cavae*,

which pour their contents into the right auricle of the heart; the venous blood is thence propelled into the right ventricle, from which the pulmonary artery arises, transmitting it through the lungs, whence it is returned by the pulmonary vein into the left auricle, which transmits it to the left ventricle, from which issues the aorta as aforesaid. So that the right cavities of the heart receive venous blood, and transmit it through the lungs, whence it returns to the left side of the heart, in the arterial state. In the lungs the blood is infinitely subdivided, and spread over a very large surface, in vessels so delicate as to admit of the operation of the atmospheric air contained in their cells; it enters the pulmonary structure in the *venous* state by the *pulmonary artery*, and returns in the *arterial* or *aërated* state, by the *pulmonary vein*. It now remains to examine the changes which the blood undergoes during pulmonary circulation.

Respiration is the process of receiving a quantity of air into the lungs, whence, after having been retained a short time, it is again expelled in the action of expiration: and, if now examined, a portion of its oxygen is found exchanged for carbonic acid, and it is more or less loaded with aqueous vapour. The nitrogen of the air probably remains passive, although from Dr. Edwards's experiments there appears to be some doubt upon this subject, for sometimes it appeared to be emitted, and sometimes absorbed in small quantities by the blood. (*De l'Influence des Agens Physiques sur la Vie*, 1824.)

Obvious circumstances render it very difficult to ascertain the quantity of air taken into the lungs at each natural inspiration, as well as the number of respirations made in a given time; the former is, perhaps, about 15 or 16 cubic inches; and the latter about 20 in a minute.

It has been by some supposed that the air suffers an absolute diminution of bulk, but the experiments that have been adduced to prove this, can, I think, scarcely be regarded as satisfactory; it seems, on the contrary, most probable that the *volume* of air expired is exactly equal to that inspired, and consequently the only chemical change that is evident is the substitution of carbonic acid for a portion of its oxygen*. The quantity of carbonic acid emitted at each expiration, varies at different periods of the day, and probably also in different individuals; it appears at its maximum during digestion, and at its minimum in the morning, when the stomach is empty, and when no chyle is flowing into the blood. Dr. Prout has shown that fermented liquors and vegetable diet diminish the proportion of carbonic acid, and that the same thing happens when the system is affected by mercury.

The air expired after a single inspiration has generally been regarded as containing, on an average, 3·5 per cent. of carbonic acid; Messrs. Allen and Pepys, however, in their *Essay on Respiration* (*Phil. Trans.*, 1808), have estimated it at about twice that quantity; it amounted, in their experiments, to between 26 and 27 cubic inches per minute, a considerable quantity when we reflect upon the comparative proportion of

* Dr. Edwards thinks that a portion of air disappears, but that it is very variable in its amount. (Bostock, *Physiology*, ii. 101.)

carbon existing in our food, and the other means of escape which it has from the body.

The following table shows the results of several experimentalists in reference to the average quantity of air required for respiration, and of carbonic acid produced by man. (GMELIN.)

	Of oxygen required in 24 hours.		Carbonic acid produced in 24 hours.		Weight of evolved Carbon.
	Cub. inches.	Grains.	Cub. inches.	Grains.	Grains.
Lavoisier and Seguin	46037	15661	14930	8584	2820
Menzies	51480	17625			
Davy	45504	15751	31680	17811	
Allen and Pepys	39600	13464	39600	18612	

The aqueous vapour contained in the expired air is probably partly secreted by the exhalants distributed over the surface of the air-vessels of the lungs, partly derived from the humidity of the mouth, fauces, and trachea, and partly evaporated from the blood. Attempts have been made to estimate its quantity, but without success; perhaps the nearest estimate is about 3 grains per minute; it is certainly liable to much variation. It is estimated by Menzies to amount to 2880 grains in the 24 hours; by Abernethy, to 4320; by Thomson, to 9120; by Hales, to 9792; and by Lavoisier, to 13,704 grains.

It has been above stated that the whole of the venous blood is propelled through the vessels of the lungs, where it is subjected to the action of the air; the chyle is of course carried along with it, and when it returns by the pulmonary vein to the left side of the heart, it has undergone a considerable change in appearance, having lost its dingy colour, and acquired a fine florid red; the chyle also has become perfect blood. The change of colour is evidently owing to the action of the air, which takes place through the thin coats of the circulating vessels, and the end thus attained is the removal of the carbonic acid from the venous blood. The only chemical difference, then, which can be satisfactorily detected between arterial and venous blood, is the existence of a certain excess of carbon, or of carbonic acid, in the latter; when this is abstracted, and oxygen substituted for it, the blood is fitted for the renovation of parts, for the formation of secretions, and for the sustenance of life by its action on the cerebral system; for although the heart does not directly refuse to circulate venous blood, torpor ensues when blood, not aerated, passes into the vessels of the brain.

It has already been shown that the blood suffers very important changes in the kidneys and liver; the function of *perspiration* also must be considered as connected with an alteration of the circulating fluid, for moisture, carbonic acid, and minute quantities of acid, and of saline and animal matter, among which are acetic or lactic acid, acetate and hydrochlorate of ammonia, and chloride of sodium, are evacuated by the cutaneous vessels. This quantity of humidity is sometimes very considerable, especially during exercise in warm weather, and it probably contributes materially to diminish the temperature of the body; a portion of water, however, is at all times passing off by the skin, as may be seen by putting the hand into a dry and cold glass, which soon be-

comes dimmed by the condensation of vapour: this is termed *insensible perspiration**.

Different animals require very different quantities of oxygen for the purposes of respiration. Man, and warm-blooded animals, consume the largest quantity; the amphibious tribes not only require less, but can breathe in an atmosphere which will not support the life of the former; and many insects take such small quantity, as sometimes to have been supposed capable of living without air, which is not the case. In the production of carbonic acid, all animals agree; and, consequently, the nature of the deterioration suffered by the air is similar throughout the animal creation.

Fishes breathe the air which is dissolved in water; they therefore soon deprive it of its oxygen, the place of which is supplied by carbonic acid; this is in many instances decomposed by aquatic vegetables, which restore oxygen, and absorb the carbon; hence the advantage of cultivating growing vegetables in artificial fish-ponds. It has been ascertained by Biot, and verified by others, that the air-bladders of fish that live in very deep water, are filled with a mixture of oxygen and nitrogen, in which the former greatly preponderates; but in fish that are taken near the surface, the nitrogen is most abundant. In the *Trygla lyra*, always caught in very deep water, the air-bladder contained 87 per cent. of oxygen: in the carp and roach, according to Fourcroy and Priestley, the air-bladder contains little else than nitrogen. (Biot, *Mémoires d'Arcueil*.)

The production of *animal heat* is perhaps the most recondite of all the functions; the power appears to belong to all animals, though to some in a very inferior degree. The higher orders of animals always maintain a temperature of about 100°; it varies a little in different parts of the body, the extremities and surface being a degree or two colder than the interior vital organs. This temperature is probably very little affected by external circumstances, a hot or cold atmosphere producing no corresponding change in the heat of the circulating blood.

When the chemical changes that take place during respiration had been inquired into, and when it was found that the capacity of carbonic acid for heat was less than that of oxygen, it was supposed that the conversion of oxygen into carbonic acid was the cause of the rise of temperature; and as the heat of the lungs does not exceed that of other

* According to Anselmino, as quoted by Tiedemann and by Berzelius, the dry residue of human perspiration contains

Saline matters, chiefly calcareous,	2
and insoluble in water and in alcohol	
Substances soluble in water, but insoluble in alcohol, comprising animal matter and sulphuric salts	21
Common salt and extractive matter soluble in dilute alcohol . .	8
Extractive matter, lactic acid, and lactates, soluble in anhydrous alcohol	29

100

The relative proportion of solid matter to that of the water, in sweat, varies according to Thenard, from 0.5 to 1.25 per cent. (*Ann. de Ch.*, lix. 262.) Some peculiar matters are occasionally thrown off by the skin, giving rise to coloured perspiration. I have heard of a case in which a man's linen was thus tinged blue; and Dr. Williams mentions the case of a lady whose perspiration, when profuse, dyed the clothes on some parts of her person, particularly the wrists and neck, of a bright crimson colour, but without any marks of blood; this was supposed by Dr. Prout to be caused by sulphocyanate of iron.

parts, it was asserted that the air was absorbed by the blood, and that the production of carbonic acid, and consequent evolution of heat, took place gradually during the circulation. To these opinions many strong objections have from time to time been urged by different physiologists, but their complete subversion followed the researches of Sir B. Brodie (*Phil. Trans.*, 1812), who found that the heart was capable of retaining its functions for some hours, and of carrying on circulation, in a decapitated animal, and consequently independent of the influence of the brain, when respiration was artificially carried on. Under these circumstances it was observed, that although the change of blood from the venous to the arterial state was apparently perfect, heat was not generated, for the animal cooled regularly and gradually down to the atmospheric standard. In more than one instance I examined, at his request, the expired air, and found that it contained as much carbonic acid as was produced by the healthy animal; so that here, circulation went on, there was the change of oxygen into carbonic acid, and the alteration of colour in the blood, and yet heat appeared not to be generated*.

In these cases, a period was also put to the secretory functions; and it has been observed by other physiologists, that if the nerves that supply any of the glands are injured or divided, there is a corresponding change or suspension of their secretion. Electricity has sometimes been supposed to have some connexion with the nervous influence, and the fact of some of the secretions being alkaline, while others are acid, (corresponding to negative and positive influence,) has been adduced in favour of the supposition (*Phil. Trans.*, 1809, p. 385); but experiment has gone little way to sanction such a notion; and although it has been proved that the *nervous influence* contributes to the generation of heat in animals, and that it presides over the phenomena of secretion, as well as of sensation and voluntary motion, neither the actual cause of this influence, nor the mode in which it operates, have been ascertained.

* Upon this subject Dr. Turner (*Elem. of Chemistry*, 5th edition, 983,) makes the following remarks: Were these experiments rigidly exact they would lead to the opinion that no caloric is evolved by the mere process of arterialization; this inference however cannot be admitted for two reasons; first, because other physiologists, in repeating the experiments of Brodie, have found that the process of cooling is retarded by artificial respiration; and secondly, because it is difficult to conceive why the formation of carbonic acid, which uniformly gives rise to increase of temperature in other cases, should not be attended, within the animal body, with a

similar effect. It may, hence, be inferred, that this is one of the sources of animal heat. It is certain, however, that the heat of animals cannot be maintained by the sole process of arterialization. Consistently with this fact, the researches of Dulong and Despretz agree in proving, in opposition to the results obtained by Lavoisier and Crawford, that a healthy animal imparts to surrounding bodies a quantity of heat considerably greater than can be accounted for by the combustion of the carbon thrown off during the same interval from the lungs in the form of carbonic acid. (*Ann de Ch. et Ph.*, xxvi.)

APPENDIX.

I. ENGLISH WEIGHTS AND MEASURES.

THE English *troy* pound is subdivided into twelve ounces, and each ounce is equal to 480 grains. The subdivisions of the troy ounce, called *Apothecaries' weight*, are into 8 drachms, each drachm into 3 scruples, and each scruple into 20 grains. The troy ounce is also sometimes divided into 20 penny weights, of 24 grains each. These are the weights generally employed by chemists, but for philosophical purposes ambiguity is most easily avoided by employing the grain as integer: and the laboratory should be provided with good sets of weights, from 1000 grains downwards; the grain should be decimally subdivided into tenths and hundredths.

The standard of most articles bought and sold in common life is the *avoirdupois* pound, which is equal to 7000 troy grains, and is divided into 16 ounces, of 437.5 troy grains each. The *avoirdupois* ounce is legally divided into 16 drachms, of 27.34375 grains each; but this division is rejected in all ordinary cases, in consequence of the confusion likely to result between the troy and *avoirdupois* drachm, so that the term *drachm* is almost exclusively employed to denote the eighth part of a troy ounce, or 60 grains.

For measures of capacity, the *wine pint* was formerly employed, which corresponds to 28.875 cubical inches of water, at a temperature of 60°. It is subdivided into 16 ounces; the ounce into 8 drachms. Two pints make a quart, and 4 quarts a gallon.

The *ale pint* contains 35.25 cubical inches of water, at 60°.

For chemical use, the most convenient measure is the bulk occupied by the troy ounce of distilled water, which may be subdivided into 480 grains, and which is equal to 1.8047 cubical inches.

The length of the pendulum, vibrating seconds *in vacuo* in the latitude of London (51° 31' 8.4" North) at the level of the sea, and at the temperature of 62°, is = 39.13929 inches of Sir George Shuckburgh's standard scale. (KATER, *Phil. Trans.*, 1819, p. 415.)

In the following Tables are shown the subdivisions of the English troy and *avoirdupois* pounds, and of the English wine gallon, and their correspondence with the French *gramme* and *litre*.

TROY WEIGHT.

Pound.	Ounces.	Drms.	Scruples.	Grains.	Grammes.
1	= 12	= 96	= 288	= 5760	= 372.96
	1	= 8	= 24	= 480	= 31.08
		1	= 3	= 60	= 3.885
			1	= 20	= 1.295
				1	= 0.06475

AVOIRDUPOIS WEIGHT.

Pound.	Ounces.	Drms.	Grains.	Grammes.
1	= 16	= 256	= 7000	= 453.25
	1	= 16	= 437.5	= 28.328
		1	= 27.34375	= 1.7705

WINE MEASURE.

Gal.	Pints.	Ounces.	Drms.	Cub. Inch.	Litres.
1	= 8	= 128	= 1024	= 231	= 3.78515
	1	= 16	= 128	= 28.875	= 0.47398
		1	= 8	= 1.8047	= 0.02957
			1	= 0.2256	= 0.00396

The IMPERIAL GALLON, now substituted for all other measures, is one-fifth more than the old wine gallon (30 Imperial = 36 Wine), and one-sixtieth less than the old ale gallon (31.5 Imperial = 30 Ale.) It contains 10 pounds of water, of 7000 grains each (avoirdupois pounds) = 70,000 grains = 277.273 cubic inches of water at 62°.

II. FRENCH WEIGHTS AND MEASURES.

THE French metrical system is founded on a single standard of length, called a *metre*, and which is equivalent to the ten-millionth part of the arc of the meridian, extending from the equator to the pole. The length of the metre, at the temperature of 32°, as ascertained by Captain Kater (*Phil. Trans.*, 1818), is 39.37079 English inches.

The French measures increase and decrease in decimal proportions, a distinctive prefix being put to the term by which the integer is called. These prefixes are *deca*, *hecto*, *kilo*, and *myria*, taken from the Greek numerals, to express the multiplication of the integer by 10, 100, 1000, and 10,000 respectively: and *deci*, *centi*, and *milli*, from the Latin numerals, to express the division of the integer by 10, 100, or 1000; as in the following table:—

	Metres.		Metre.
1 Myriametre	= 10000	1 Metre	= 1
1 Kilometre	= 1000	1 Decimetre	= 0.1
1 Hectometre	= 100	1 Centimetre	= 0.01
1 Decametre	= 10	1 Millimetre	= 0.001

The metre is the integer of the measure of length, and from it all measures of surface, capacity, and weight, are deduced as follows:—

For square dimensions, the metre, or its parts squared, are employed. When used for measuring land, the term *are* is adopted, which is a decametre squared. An *hectare*, or 100 *ares*, is about equal to 2 English acres.

For the integer of the measure of capacity, the cubed decimetre is employed, under the name of *litre*, which is about equal to $2\frac{1}{8}$ English wine pints.

For the integer of the measure of weight, the weight of a cubic centimetre of distilled water, at 32° , has been adopted: it is called a *gramme*, and is equal to 15·4 English grains.

The following are the principal tables of French Weights and Measures, which will be found useful in the laboratory. In *Appendix II.* of *AIKIN'S Dictionary*, the reader will find several others, showing the relation of the French to the English standards.

MEASURES OF LENGTH.

		English inches.					
Millimetre . . .	=	·03937					
Centimetre . . .	=	·39371					
Decimetre . . .	=	3·93710					
Metre	=	39·37100					
Decametre . . .	=	393·71000	Mil.	Fur.	Yds.	Feet.	In.
Hecatometre . .	=	3937·10000	= 0	0	10	2	97
Kilometre . . .	=	39371·00000	= 0	0	109	1	1
Myriometre . . .	=	393710·00000	= 0	4	213	1	10·2
			= 6	1	156	0	6

MEASURES OF CAPACITY.

		Cubic inches.				
Millilitre . . .	=	·06102				
Centilitre . . .	=	·61028				
Decilitre	=	6·10280				
Litre	=	61·02800	<i>English.</i>			
Decalitre	=	610·28000	Tons.	Hogs.	Wine G.	Pints.
Hecalitre	=	6102·80000	= 0	0	0·	2·1133
Kilolitre	=	61028·00000	= 0	0	26·419	5·1352
Myriolitre . . .	=	610280·00000	= 1	0	12·19	
			= 10	1	58·9	

MEASURES OF WEIGHT.

		English grains.			
Milligramme . . .	=	·0154			
Centigramme . . .	=	·1544			
Decigramme . . .	=	1·5444			
Gramme	=	15·4440			
Decagramme . . .	=	154·4402	<i>Avoirdupois.</i>		
Hecatogramme . .	=	1544·4023	Poun.	Oun.	Dram.
Kilogramme . . .	=	15444·0234	= 0	0	5·65
Myriogramme . . .	=	154440·2344	= 0	3	8·5
			= 2	3	5
			= 22	1	2

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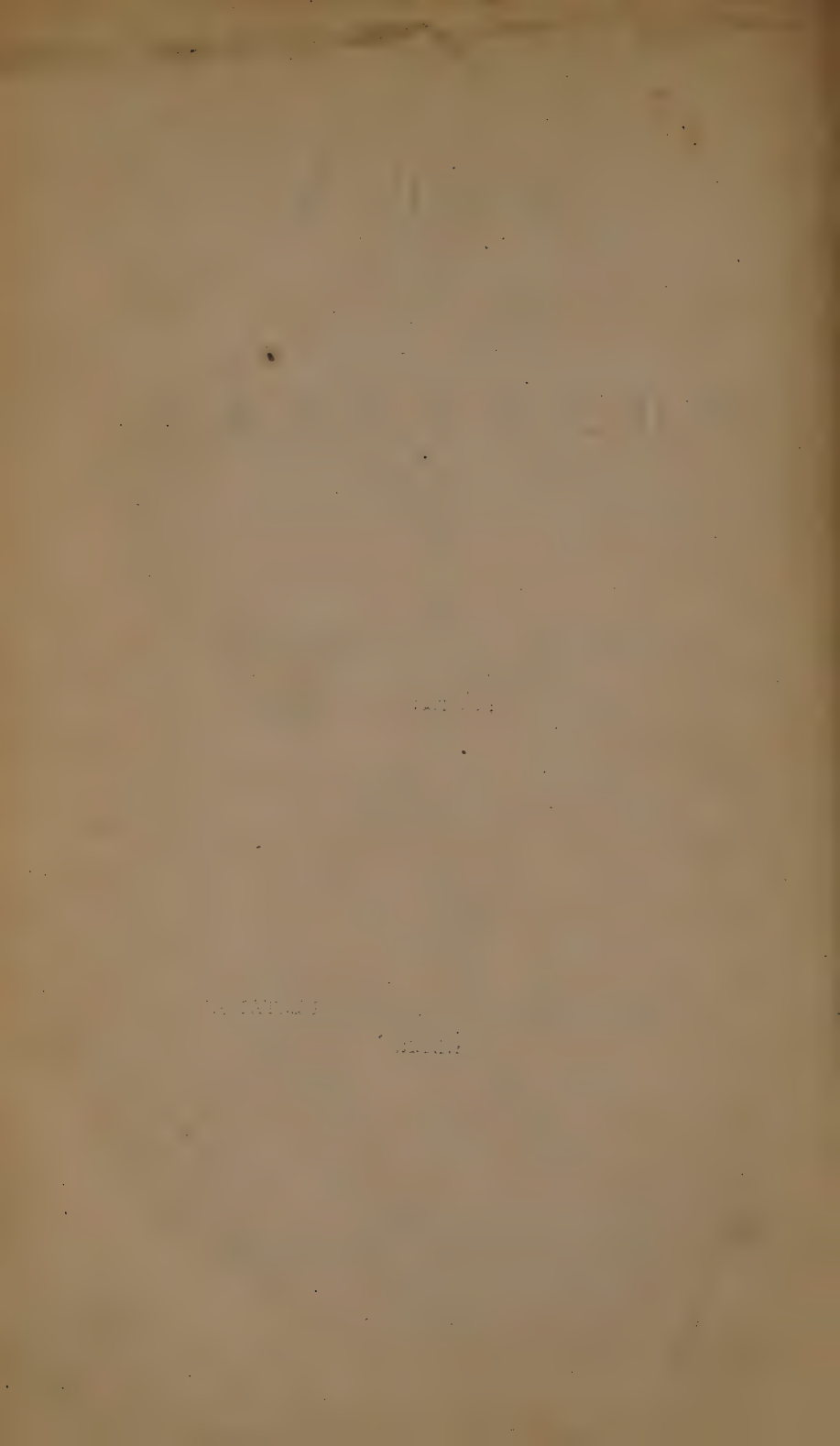
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This is an inquiry, however, upon which we do not intend to enter. We may content ourselves with remarking, that the present revival may be traced, in a great measure, to the efforts of a few individuals, who have, at different times within the last half century, given to the world, in the form of illustrated works, the result of their labours and researches in this department of art. The beautiful and elaborate works of Carter, Britton, and Pugin, and, above all, the excellent and practical work of Rickman, have contributed, more than any other cause, to the general diffusion of this taste. But the works just mentioned, with the exception of the last, and some of those of Pugin, have, we contend, contributed more to excite an interest in the subject, and a desire for information, than to furnish materials for acquiring the knowledge sought. The great want at the present time is a sufficient collection of examples on which to form correct principles of theory, and a sure guide for modern practice.

Before we can hope to attain a true knowledge of the principles which guided the ecclesiastical architects of the Middle Ages, or imbibe the spirit which enabled them to design such glorious structures, we must first patiently study the remains which sacrilegious hands have spared to us: we must be content to imitate before we can hope to create. By frequent and continued contemplation of models of acknowledged excellence, our taste will be insensibly cultivated, and our minds led imperceptibly to imbibe those principles, and to acquire that state of susceptibility to beauty, which is essential to the appreciation and production of works in every department of the Fine Arts.

Though abundant in many parts of this country, these venerable remains cannot be studied to any extent but at great expense, and by few individuals; it becomes therefore a matter of extreme importance to all who desire the revival of genuine Church Architecture, to be thus enabled, through the medium of descriptions and illustrations, to study these ancient remains at a cost little more than nominal.

The object of the present work is to furnish, at a cheap rate, illustrations of the best specimens of the Ecclesiastical Remains in this country, confining them to such as shall be excellent in design, adapted to modern practice, and not too elaborate or expensive in execution.

It is not proposed merely to interest and inform the antiquary, but to furnish correct and genuine examples of ordinary *Parish Churches*, erected on true Anglican principles. It must not, therefore, be expected that the historical portion of the work will be very comprehensive, or exhibit elaborate research, further than may be necessary to elucidate the character, style, and date of the examples given; first, because it would not lie within the scope, or accord with the nature of the work; and, secondly, because many of the Churches selected afford but scanty materials for such disquisitions.

The specimens will chiefly consist of such Country Churches as are best suited for imitation, and most adapted to the wants of the present age, though some of them are comparatively little known. Many of the examples hitherto chosen for publication are either remarkable for their splendour, and therefore not of much *practical* value, or interesting from their great antiquity, but possessing little or nothing suited for imitation, belonging as they generally did, to an age and state of society widely different from our own.

Among the subjects given will be some of great excellence, which have within a few years gone into decay, but of which drawings were made while they were in existence. Specimens of such ancient Stained Glass and Church Furniture as may be deemed of sufficient excellence, will also occasionally be given.

The Work will be published in Numbers, from one to three of which will be devoted to each Church. A condensed History of the different Styles of Christian Architecture will be added, together with a copious Index, in which the examples given will be arranged both alphabetically and chronologically.

Instructions in Household Matters; or, the Young Girl's Guide to Domestic Service. Written by A LADY, with an especial view to Young Girls intended for Service on leaving School. With Wood-Cuts. 1s. 6d.

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Numbers I. to V. are already published, price 8d. each; to be continued.

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Collections in Popular Literature.

IT has been frequently suggested to the Publisher, that he might render an acceptable service to the friends of Education, and greatly assist those who desire to promote the intellectual amusement of the people, by producing a series of Popular Books, at low prices, calculated, by their unexceptionable tendency, for general use in families; from which School Libraries might be formed, Reward Books selected, and Lending Libraries supplied; which, on account of their convenient form and size, would be welcome as Fireside and Travelling Companions; books, in short, which might be found instructive and entertaining wherever introduced.

These suggestions he is now carrying out, in compliance with certain conditions, namely, that the works produced shall be unexceptionable in subject and in treatment; that the series be sufficiently varied to meet the requirements of all classes of readers; and that each book shall be complete in itself, and procurable for a small sum.

The COLLECTIONS IN POPULAR LITERATURE will, therefore, embrace most of the features of an Encyclopædia, though the subjects will not be divided into fragments, or scattered over many volumes; each subject being treated with fulness and completeness, and its information brought up to the present time.

The Plan will embrace new and improved Editions of certain Standard English books, but the majority of the works will be newly written, translated, compiled, or abridged, for the present purpose; and the volumes will appear from time to time in sufficient variety to extend simultaneously, and in due proportion, the various branches of Popular Literature. The whole will be prepared with an especial view to the diffusion of sound opinions—to the promulgation of valuable facts and correct principles—and to the due indulgence of general literary taste.

It is not intended that this series shall form a periodical, according to the strict acceptation of that term. Several works are already published, and others will quickly follow; they will all be uniformly bound in cloth and lettered. There will be no necessary connection between the various works, except as regards general appearance, and each, being complete in itself, may be had separately; nevertheless, the volumes, distinct, yet uniform in their object, will together form a valuable library, and may be collected and classified under the following heads:

I. Popular History.

Under the comprehensive title of History, we purpose giving an extensive series of interesting and instructive works. Among these will be carefully-considered narratives of some of those moral tempests which have so often agitated the world, when men have continued a long course of disobedience to the laws of God and the recognised laws of man. We shall make it our business to record the change of a dynasty, the rise and career of a monarch, a usurper or a ruler, whose actions have thrown a new aspect on the political

institutions of a country; we shall trace the rise and progress of great commercial or manufacturing enterprises, whereby the wealth and prosperity of a nation have been obviously increased; we shall notice the train of events whereby the prevalent or established religion of a country has been changed. These and other subjects of a like character will enable us to bring up many stores from a mine peculiarly rich in instructive and entertaining matter.

It is of course impossible, in such a notice as this, to include all the features of so important a division of our COLLECTIONS IN POPULAR LITERATURE as History; but some idea may be formed of it from the following list:

A History of the Invasion of Russia by Napoleon Bonaparte. 2s. 6d.

The Lord and the Vassal: a Familiar Exposition of the Feudal System in the Middle Ages; with its Causes and Consequences. 2s.

A History of the French Revolution; its Causes and Consequences. Newly written for this Collection. By Frederica Maclean Rowan.

The Ruins of Rome and their Historical Associations; including an Account of the Modern City and its Inhabitants. *In the Press.*

The Private Life, Manners, and Customs of the Ancient Romans. From the French of D'Arnay; carefully edited, and forming a valuable work for study or amusement. *In the Press.*

Constantinople and its Historical Associations; with some Account of its Institutions and the Manners and Customs of the People.

History of the Trading Communities of the Middle Ages.

Trading Communities of Modern Times.

The Ruins of Athens and their Historical Associations; with Notices of the Modern City and its Inhabitants.

The following are in course of preparation for the Press:

A History of London, Ancient and Modern A History of the Endowed Schools of Great Britain The Incas of Peru, with some Account of the Ruins of their Greatness A popular History of the British Army A popular History of the British Navy The Sicilian Vespers.

II. Popular Biography.

One of the most useful and pleasing forms under which knowledge can be presented to the general reader is that of the Biography of distinguished men, who have contributed to the progress of that knowledge in some one or other of its various departments. But it too frequently happens, that the biographical notices of great men consist rather of personal, trivial, and unimportant details, than of a clear and broad outline of the influence which they exerted upon the pursuit and upon the age in which they were distinguished. The true object of Biography is, while tracing the progress of an individual, to show not only what result his active life has produced on the well-being of his fellow-men, but also the position which he occupies as one of the "great landmarks in the map of human nature."

Yet we are not satisfied with a biography which regards its subject in his public capacity alone: we are naturally curious to ascertain whether the same

qualities which rendered him celebrated in public, followed him likewise into private life, and distinguished him there. We regard, with interest, in his private capacity, the man who has been the originator of much public good: we look with an attentive eye on his behaviour when he stands alone, when his native impulses are under no external excitement; when he is, in fact, "in the undress of one who has retired from the stage on which he felt he had a part to sustain."

But a detail of the public and private events in the life of a distinguished man, do not alone suffice to form a just estimate of his character. The reader requires to be made acquainted with the state of a particular branch of knowledge, at the time when the individual appeared, whose efforts extended its boundaries. Without this it is impossible to estimate the worth of the man, or the blessings and advantages conferred upon society by his means.

On the other hand, in tracing the history of any particular branch of knowledge unless connected with Biography, we lose sight of individual efforts; they are mingled with the labours of others, or are absorbed into the history of the whole, and are consequently no longer individualized: hence we are likely to fail in recognising the obligations due to our distinguished countrymen, or to deprive of their just merit those of our foreign brethren, whose useful lives have influenced distant lands as well as their own.

With these views it is proposed that each Biography shall consist of three distinct portions:

- 1 The history of a particular department of knowledge, up to the time when the individual appeared by whom its boundaries were extended.
- 2 A *general* sketch of the life of such individual, with *particular* details of the improvements effected by him.
- 3 The progress of such branch of knowledge, from the date of such improvements up to our own times.

The following form part of this Division:

Smeaton and Lighthouses; a Popular Biography, with an Historical Introduction and Sequel. 2s.

Linnaeus and Jussieu; or, the Rise and Progress of Systematic Botany. 2s.

Cuvier and his Works; or, the Rise and Progress of Zoology. 2s.

Sir Joseph Banks and the Royal Society. *In the Press.*

Sir Humphrey Davy and the Safety Lamp. *In the Press.*

These will be followed by:

Brindley and Canals Watt and the Steam-Engine Wedgwood and Pottery Telford and Roads and Bridges Caxton and the Printing Press Galileo and the Telescope Sir Isaac Newton and the Progress of Astronomical Discovery Sir Christopher Wren and St. Paul's Cathedral Addison and the English Essayists Jeremy Taylor and some Account of his Times and Works Wilberforce and the Slave Trade.

Each work being a Popular Biography, with an Historical Introduction and Sequel.

III. Popular Science and Art.

When we contemplate the arts and processes of civilized life, we cannot but be struck with the vast amount of invention and ingenuity required for their gradual development. Not an article of clothing or of furniture, not an instrument, implement, or machine, could have been brought to the state in which we find it, without many successive steps of invention, due to different minds, supplied at different times, and brought to light in different countries. But in devoting several of our volumes to the Useful Arts, we shall not be unmindful of the fact, that Art is the application of Science to a practical end. It is proposed, therefore, under the comprehensive title of *Popular Science and Art*, to include portions of our knowledge of animate and inanimate nature. The object will be to assist the general reader to regard with an intelligent eye the varied phenomena of nature, to gratify the laudable desire of understanding what he sees, and of preparing him in some measure to enter more fully upon the study of a given subject. In this way, it is hoped to effect a useful purpose, by connecting Science and the Useful Arts; for "it is not, surely, in the country of Arkwright, that the Philosophy of Commerce can be thought independent of Mechanics; and where Davy has delivered lectures on Agriculture, it would be folly to say that the most philosophic views of Chemistry were not conducive to the making our valleys laugh with corn."

The Useful Arts employed in the Production of Food. 2s 6d.

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The Useful Arts employed in the Construction of Dwelling Houses. 2s. 6d.

The Writing-Desk and its Contents, taken as a Text for the Familiar Illustration of many important Facts in Experimental Science. 2s.

The above works are already published in this Division, and others on the following subjects are in course of preparation:

Examples of Mechanical Ingenuity The Philosophy of the External Senses Ancient and Modern Modes of Measuring Time, with curious Illustrations of the Application of Clockwork The Rise and Progress of Agriculture The Natural History of Birds and Insects injurious to Farming and Gardening The Wonders of the Microscope Mathematical Magic.

The Fine Arts will also form an interesting portion of this Division. The object will be, in a few popular histories, to trace the origin, rise, and progress of Sculpture, Painting, Engraving, Music, &c., and their influence on mankind.

IV. Popular Voyages and Travels.

Few subjects are more attractive than the narratives of celebrated travellers. Although they tell us of beings who speak another tongue, inhabit a different clime, differ altogether from ourselves in manners, customs, dress, and institutions—yet the sympathy which man feels for his fellows makes us delight in all the details which talent and enterprise procure for us. The personal narrative of the traveller has also a great charm; we seem to participate in his dangers, excitements, and pleasures; we add to our knowledge in his company; and the truth and sincerity which pervade the narrative, make us feel a personal interest in the narrator. It is intended to reprint some of the narratives of our old English Navigators, especially those of Discoveries, which have had most influence on the progress of Geographical Knowledge. It will not be an objection that these eminent men lived at a period of time distant from our own; for their narratives are full of truth, told with plain simplicity.

But the important labours of modern travellers will not be forgotten. In describing several interesting portions of the earth's surface, we shall avail ourselves of the most trustworthy individuals, and by a careful comparison of statements and details, we hope to present graphic descriptions of some of the most celebrated countries of the world; as well as of those which have only of late years been explored. Many voyages of discovery have had their proceedings recorded in large quartos, the price of which places them above the reach of the general reader, while their scientific details render them unfit for popular use: a digest of these works, containing an epitome of the lighter portions, and the results of the scientific discoveries, may prove acceptable.

The following works are in a forward state for publication:

The Life, Adventures, and Discoveries of Captain William Dampier; including a History of the Buccaneers of America.

Captain Cook and the Circumnavigation of the Globe.

An Overland Journey and a Steam Voyage to India.

Voyages and Discoveries in the South Polar Regions.

Voyages and Discoveries in the Northern Polar Regions.

Voyages and Discoveries in Australia and Polynesia.

To these will be added digests of Travels and Adventures in various Countries of the Old and New Worlds.

V. Popular Tales and Fiction.

The design of this Collection embraces many favourite old works, which, though containing much that has instructed and delighted our predecessors; are, nevertheless, but ill adapted in their original form for general perusal. Among these may be reckoned some works of fiction, the excellencies of which are often obscured by a grossness of style not uncommon at the time when they were composed, but which justly excludes them from family reading in the present day. Such works would be acceptable if freed from objectionable passages; and in undertaking to accomplish this reform, without detriment to the spirit of the original, the Publisher relies on the approbation of a large class of persons, who will thus be enabled to place in the hands of the young, purified editions of those romantic and interesting tales which are naturally sought for by youthful readers, whose hands they might otherwise reach, tainted with their original impurities. Every work will be prepared for this series by a careful editing, in order to suit the general tone of thought, principle, and feeling which will pervade the whole Collection, and no work will be admitted, the name of whose author is associated with considerations painful to Christian feeling, good taste, or propriety.

Among the new works intended to be included in this Division, may be mentioned a series of tales, illustrative of the manners and customs of the people of different climes.

The Merchant and the Friar; or, Truths and Fictions of the Middle Ages. By SIR FRANCIS PALGRAVE. A New Edition, revised. 3s.

The Life and Adventures of Peter Wilkins, a Cornish Man. Carefully revised and corrected. 3s.

The most Delectable History of Reynard the Fox, and of his Son Reynardine. A revised version of an old Romance. 2s.

Van-ti, the Chinese Magistrate; and other Tales of Other Lands. 2s.

Norah Toole, a Tale of Ireland; and other Tales illustrative of National and Domestic Manners. 2s.

Stories of Emigrants, or, Life in Canada, the United States, and Australia.

Carlo the Courier, or the Travellers in Italy; Annette Darville, or, the French Market Girl; and Herman Stult, or the German Peasant. Tales illustrative of Life on the Continent. In one Volume.

The Life and Adventures of Robinson Crusoe, newly revised; with an Introduction, and numerous Illustrations.

VI. Popular Miscellanies.

Under this head will be published, works of a miscellaneous nature which do not fall strictly under any of the foregoing Divisions, or which may include several of those Divisions. Among the former may be mentioned a short series of works on in-door and out-door amusements, the object of which is to furnish young persons with sources of amusement, innocent in their kind, and healthful in their application both to mind and body. Among the in-door amusements may be mentioned a volume which is nearly ready for publication on the game of Chess. Experience has shown that where Chess is introduced as an amusement into families and schools, it exerts a highly beneficial influence, by exciting a taste for more exalted sources of recreation than are afforded by *games of chance*, which so far from producing a beneficial influence on the mind, are apt to disturb the temper, excite animosity, and foster a spirit of gambling. Chess, on the contrary, is an effort of pure skill; it gives healthy exercise to the mental powers; it requires caution and forbearance on the part of both players; it leaves the victor satisfied with having won the game without the additional stimulus of 'a stake;' and it entails no humiliation on the vanquished, but rather prompts him to greater exertions. We propose, therefore, to give the history and antiquities of the game of Chess, together with a series of Easy Lessons, the object of which will be to make the young student acquainted with a few of the leading features of the principal openings, that he may form some idea of the richness of the territory of Chess, and to add a selection of Chess Problems. Chess Problems form one of the most attractive departments of the game; they enable us, more perhaps than anything else, to appreciate the subtle skill and resources of a first-rate player, and tend to elevate Chess to the rank of mathematical science.

Among the works which include several of the foregoing Divisions, is one in four volumes, illustrating the Progress of the Year, wherein the information given is arranged under the form of Daily Readings. All the varied phenomena of nature, the animals, the plants, the minerals, assume different phases, according to the means and acquirements of the observer, the progress of science, and the climate under which the descriptions are given. As science advances, the descriptions of naturalists admit of modification and addition in order to keep pace with the progress of discovery; hence our Year-books require renewal from time to time. The present is an attempt to furnish a seasonal account of the natural phenomena of the year, in conformity with the present state of knowledge. The work, however, will not be confined to natural history, but will be varied with notices of the arts, antiquities, manners and customs, of our native country; choice selections from our prose writers and poets; and a series of papers expressly adapted for Sunday reading, so that on whatever day, and at

whatever season, the book be taken up, something appropriate of an instructive and amusing nature may be found, calculated either for family reading or solitary perusal, as a fireside manual, or a travelling pocket companion.

The following are among the works intended for this portion of the COLLECTIONS :

Chronicles of the Seasons, or, the Progress of the Year; being a Course of Daily Instruction and Amusement from the Popular Details of the Natural History, Science, Art, Antiquities, and Biography of our Father-Land. In Four Books.

Book the First, containing the Months of January, February, and March.

Book the Second, containing April, May, and June.

Book the Third, containing July, August, and September; 3s. 6d. each.

The History, Antiquities, and Curiosities of the Game of Chess; including a Selection of Games, illustrative of the various Openings, Analysed and Explained for the use of Young Players; together with a Choice Selection of Chess Problems.

The Sea—the Highway of the World; or the History and Practice of Navigation in Ancient and Modern Times, familiarly explained.

The Houses of all Nations; or, some Account, Historical and Descriptive, of the Progress of National and Domestic Architecture in all Parts and Ages of the World.

The Games and Sports of the Ancients and Moderns.

An Account of Shipwrecks, Fires, and other Calamities, at Sea.

The works named in this Prospectus are those only which will immediately appear. Other works will from time to time continue to be added to each of the several Divisions of the COLLECTIONS IN POPULAR LITERATURE.

